Numerical Problems in Solid State Physics

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M.A. Wahab

Narosa

Contents

Preface *v*

Units of Measurements *vii*

Physical Constants *ix*

Conversion Factors *xi*

1. Basic Crystallography **1.1-1.43**

2. Atomic Shape and Size **2.1-2.26**

3. Atomic Bonding and Packing **3.1-3.32**

4. Crystal Imperfections and Atomic Diffusion **4.1-4.37**

5. Lattice Vibrations and Thermal Properties of Materials **5.1-5.26**

6. Diffraction of Waves and Particles **6.1-6.46**

7. Electrical Properties of Materials **7.1-7.30**

8. Band Theory and Fermi Surfaces **8.1-8.26**

9. Semi conducting Properties of Materials **9.1-9.25**

10. Dielectric and Optical Properties of Materials **10.1-10.19**

11. Magnetic Properties of Materials **11.1-11.12**

12. Superconducting Properties of Materials **12.1-12.9**

Index *I.1*

CHAPTER 1

Basic Crystallography

IMPORTANT FORMULAE

1.1 PLANE AND SPACE LATTICES

(a) In a plane lattice, any two points connected through a translation vector T is given by

$$T = n_1 a + n_2 b$$

where n_1 and n_2 are arbitrary integers, when putting together in the form $[n_1 n_2]$ gives the direction of the translation vector T in the given lattice and a and b are primitive translation vectors along x and y axes.

(b) In a space lattice, any two points connected through a translation vector T is given by

$$T = n_1 a + n_2 b + n_3 c$$

where n_1, n_2 and n_3 are arbitrary integers, when putting together in the form $[n_1 n_2 n_3]$ gives the direction of the translation vector T in the given lattice and a, b and c are primitive translation vectors along x, y and z axes.

(c) The magnitude R of the resultant translation vector between any two points (in a plan lattice) is determined by the formula

$$R = \sqrt{P^2 + Q^2 + 2PQ \cos \phi}$$

where $P = n_1 a$ and $Q = n_2 b$ are measured in terms of the primitive vectors a, b and ϕ is the angle between them.

Similarly, in a space lattice,

$$R = \sqrt{P^2 + Q^2 + S^2 + 2PQ \cos \alpha + 2QS \cos \beta + 2SP \cos \gamma}$$

where $P = n_1 a$, $Q = n_2 b$, $S = n_3 c$ and α, β, γ are the angles between PQ, QS and SP, respectively.

1.2 CONSTRUCTION OF WIGNER-SEITZ UNIT CELL

We adopt the following procedure to construct a Wigner-Seitz unit cell in general.

(a) For a given lattice, select a lattice point as the origin and draw lines to connect this point with all nearby lattice points.

(b) Draw new lines (in a plane lattice) or planes (in a space lattice) bisecting each of the previous lines (planes). The smallest area (in 2-dimensions) or volume (in 3-dimensions) enclosed in this way gives the Wigner-Seitz primitive unit cell.

1.3 DENSITY OF ATOMS IN CRYSTALS

(a) The volume atomic density of the crystal material is given by

$$\rho_V = \frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}} = \frac{Mn}{N} \cdot \frac{1}{V} = \frac{Mn}{Na^3}$$

where

M = Atomic weight or molecular weight

n = Number of atoms per unit cell (or No. of formula unit)

$N = 6.023 \times 10^{26}$ (Avogadro's number in SI system)

a = Side of the cubic unit cell

Mass of the unit cell is given by

Mass of the unit cell = No. of atoms in the unit cell × mass of each atom

$$= n \times m$$

Mass of an atom (m), in turn, is given by

$$m = \frac{\text{Atomic mass (or Molar mass)}}{\text{Avogadro's number}} = \frac{M}{N} \text{ kg}$$

(b) Planar atomic density is given by

$$\rho_p = \frac{\text{Number of atoms in the given plane}}{\text{Area of the given plane}} = \frac{n'}{A} = \frac{nd}{V}$$

where

n = Number of atoms in the unit cell

d = Interplanar spacing

V = Volume of the unit cell

(c) Linear atomic density is given by

$$\rho_l = \frac{\text{Number of atoms in the given direction (line)}}{\text{Length of the given line}} = \frac{n}{L}$$

1.4 MILLER INDICES OF ATOMIC SITES, PLANES AND DIRECTIONS

(a) In order to locate the atomic sites (positions) in cubic unit cells, we use rectangular x, y and z axes. The positive x-axis is taken as the direction coming out of the paper. The positive y-axis is the direction along right side of the paper, and the positive z-axis is the direction to the top as shown in Fig. 1.1a. Negative directions are just opposite to their counterparts. The atomic positions in the unit cells are located at unit distances along the x-, y- and z- axes as indicated in Fig. 1.1b. For example, the position coordinates for the atoms in a simple cubic unit cell are shown in Fig. 1.1c. The atomic positions of the eight corner atoms are:

[[000]] [[100]] [[010]] [[000]]
[[111]] [[110]] [[101]] [[011]].

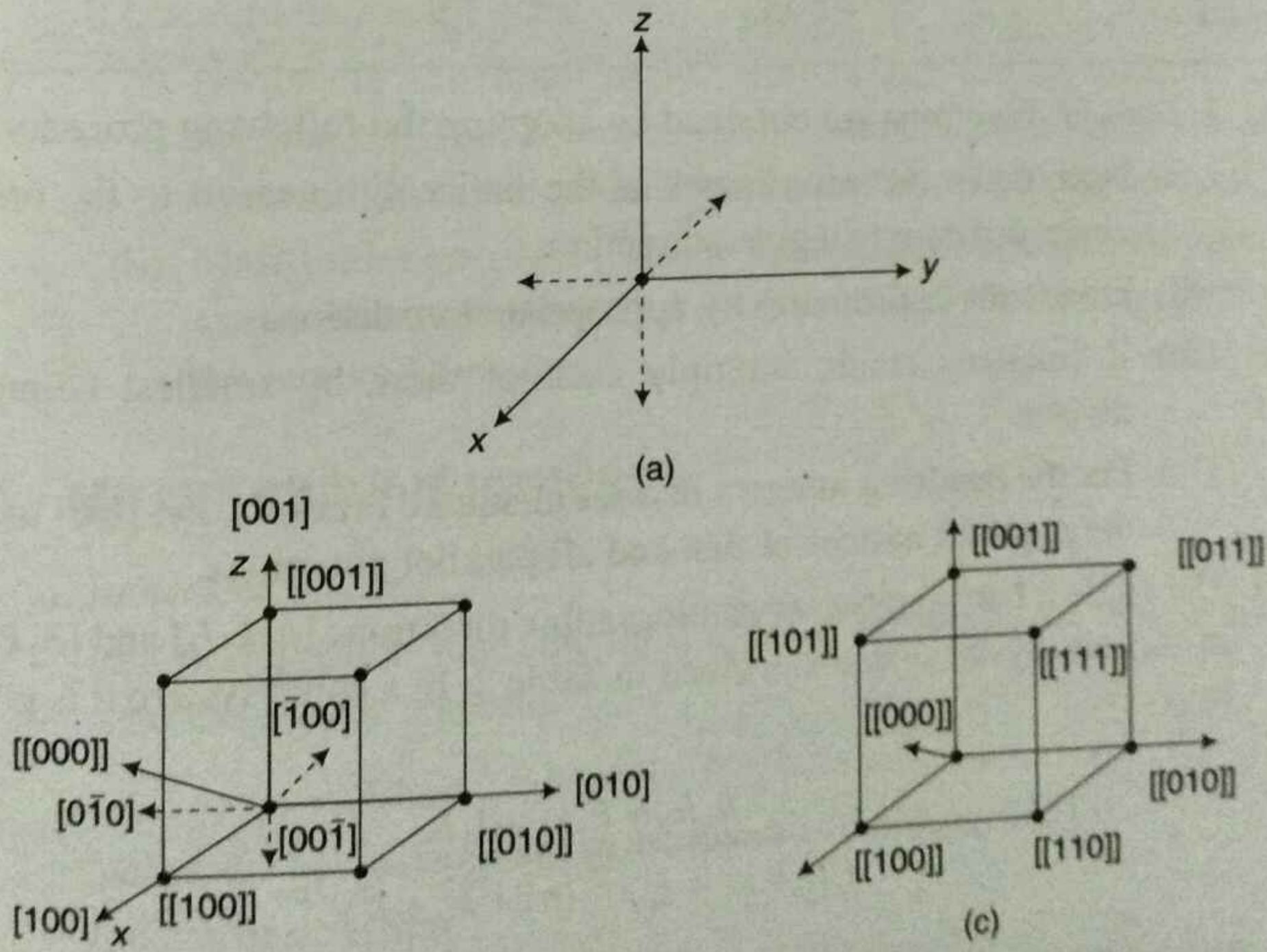


Fig. 1.1 (a) Orthogonal axes, (b) site indices and principal directions, (c) site indices in a cube

(b) Indices of a plane are obtained by adopting the following procedure

(i) Determine intercepts of the plane along x, y and z axes in terms of lattice parameters.

(ii) Divide these intercepts by the appropriate unit translations (see Table 1.1)

(iii) Note their reciprocals

(iv) If fractions result, multiply each of them by the smallest common divisor.

(v) Put the resulting integers in parenthesis, i.e. (hkl) to get the required indices of that and all parallel planes.

Table 1.1 The unit translation for low index directions of cubic system

Family	*Unit translation*		
	P	*I*	*F*
<100>	a	a	a
<110>	$\sqrt{2}a$	$\sqrt{2}a$	$\frac{a}{\sqrt{2}}$
<111>	$\sqrt{3}a$	$\frac{\sqrt{3}a}{2}$	$\sqrt{3}a$

(c) Indices of directions are obtained by adopting the following procedure

(i) Note down the coordinates of the lattice site nearest to the origin corresponding to a given direction.

(ii) Divide the coordinates by appropriate translations

(iii) If fractions result, multiply each of them by smallest common divisor.

(iv) Put the resulting integers in a set of square brackets, i.e. $[hkl]$ to get the required indices of that and all parallel directions.

(d) The angle θ between two crystallographic directions $[h_1 k_1 l_1]$ and $[h_2 k_2 l_2]$ in various crystal systems is given in Table 2. In a cubic system it is given by

$$\cos\theta = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{(h_1^2 + k_1^2 + l_1^2)^{1/2} (h_2^2 + k_2^2 + l_2^2)^{1/2}}$$

1.5 REPRESENTATION OF PLANES (DIRECTIONS) OF KNOWN MILLER INDICES

(a) Representation of Planes

(i) Take the reciprocals of the given Miller indices. They represent the intercepts in terms of axial units.

Table 1.2 Angle between two crystal directions $[h_1 k_1 l_1]$ and $[h_2 k_2 l_2]$

Crystal system	$\cos\phi$
Cubic	$\dfrac{h_1h_2 + k_1k_2 + l_1l_2}{(h_1^2 + k_1^2 + l_1^2)^{1/2}\,(h_2^2 + k_2^2 + l_2^2)^{1/2}}$
Tetragonal	$\dfrac{a^2(h_1h_2 + k_1k_2) + c^2(l_1l_2)}{\sqrt{\{a^2(h_1^2 + k_1^2) + c^2l_1^2\}\,\{a^2(h_2^2 + k_2^2) + c^2l_2^2\}}}$
Orthrhombic	$\dfrac{a^2h_1h_2 + b^2k_1k_2 + c^2l_1l_2}{\sqrt{(a^2h_1^2 + b^2k_1^2 + c^2l_1^2)\,(a^2h_2^2 + b^2k_2^2 + c^2l_2^2)}}$
Hexagonal	$\dfrac{h_1h_2 + k_1k_2 - \frac{1}{2}(h_1k_2 + k_1h_2) + \frac{c^2}{a^2}l_1l_2}{\sqrt{\left(h_1^2 + k_1^2 - h_1k_1 + \frac{c^2}{a^2}l_1^2\right)\left(h_2^2 + k_2^2 - h_2k_2 + \frac{c^2}{a^2}l_2^2\right)}}$

(ii) Mask the length of the intercepts on the respective coordinate axes each one starting from the origin. Join all the end points. The resulting sketch will represent the required plane.

(b) Representation of directions

(i) Divide the Miller indices by a number such that the resulting indices become ≤ 1. They represent the coordinates of the lattice site nearest to the origin in the given direction and lie within the unit cell.

(ii) Mark the length of the position vector along the respective coordinate axes without disconnection. Join the origin with the end point to get the required direction.

1.6 MILLER BRAVAIS INDICES

(a) Indices of Planes

In a hexagonal system, the third index is related to the first two indices according to the equation

$$i = -(h + k) \quad \text{or} \quad h + k + i = 0$$

Miller Bravais indices are symbolised as (*hkil*) or (*hk.l*).

(b) Indices of direction

Three Miller indices [HKL] and four Miller-Bravais indices [*hkil*] are connected through the following equations

$$H = h - i \qquad h = (2H - K)/3$$

$$K = k - i \quad \Rightarrow \quad k = (2K - H)/3$$

$$i = -(h + k) \text{ and}$$

$$L = l \qquad l = L$$

The Miller-Bravais indices of principal directions in the basal plane of a hexagonal crystal is shown in Fig. 1.2.

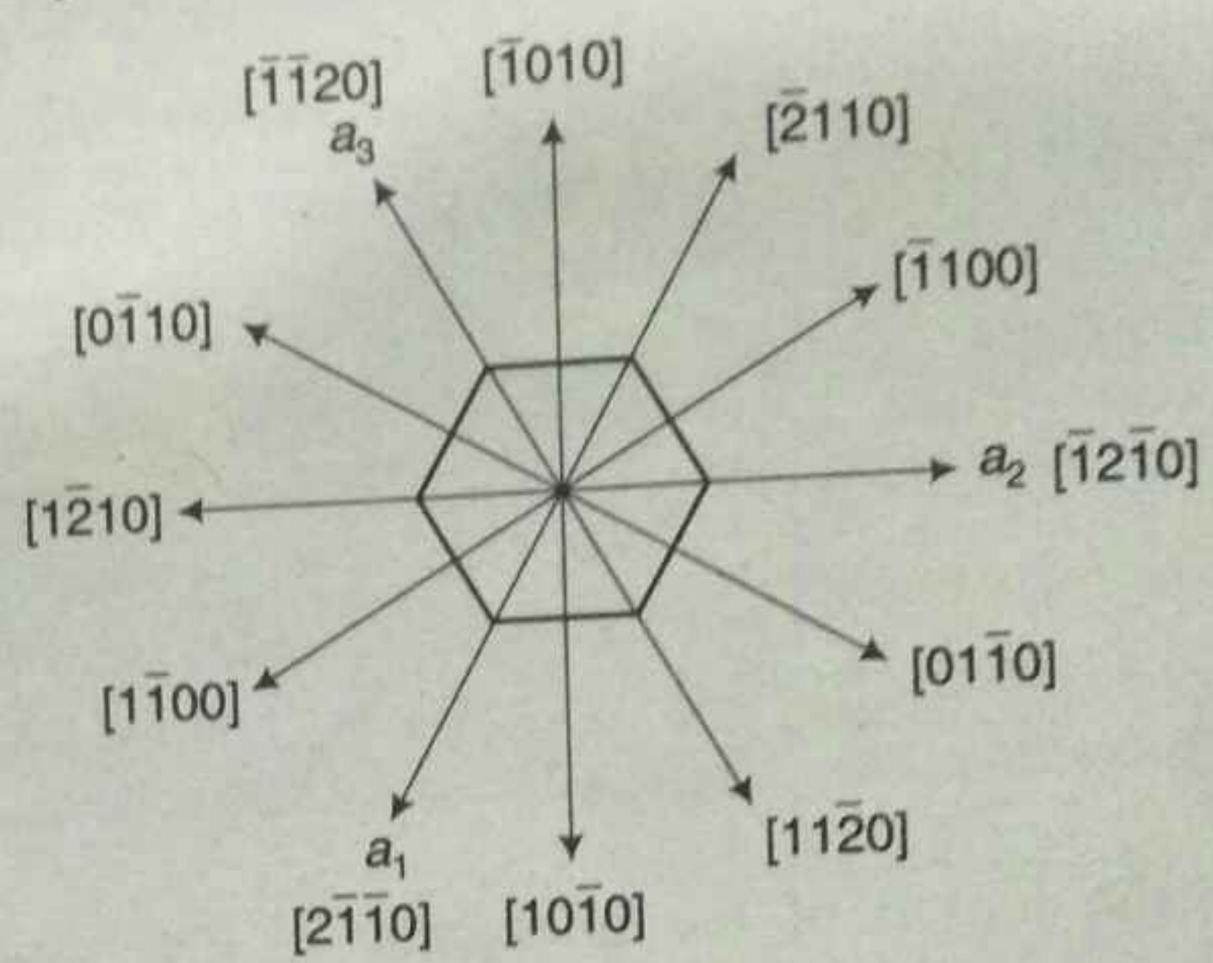


Fig. 1.2 Miller-Bravais indices of principal directions in the basal plane of hexagonal crystal system

1.7 INTERPLANAR SPACING

Interplanar spacing for various crystal system is provided in Table 1.3. For a cubic system it is given by

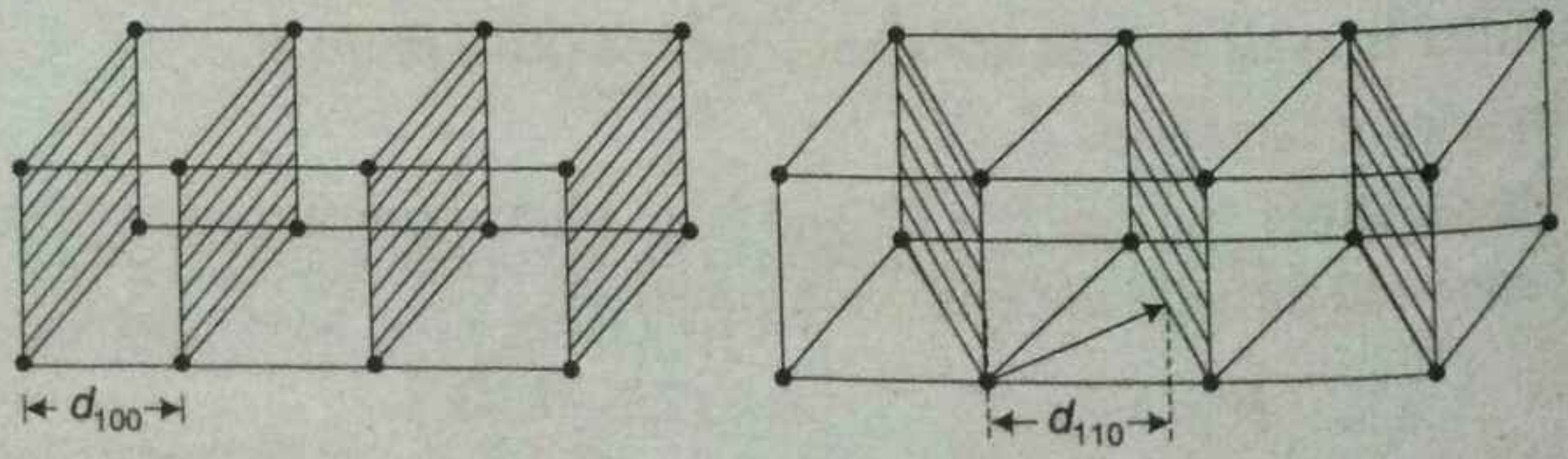
$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$

where a is the side of the cube

(a) Simple cubic lattice

$$d_{100} = a \quad d_{110} = \frac{a}{\sqrt{2}} \quad \text{and} \quad d_{111} = \frac{a}{\sqrt{3}}$$

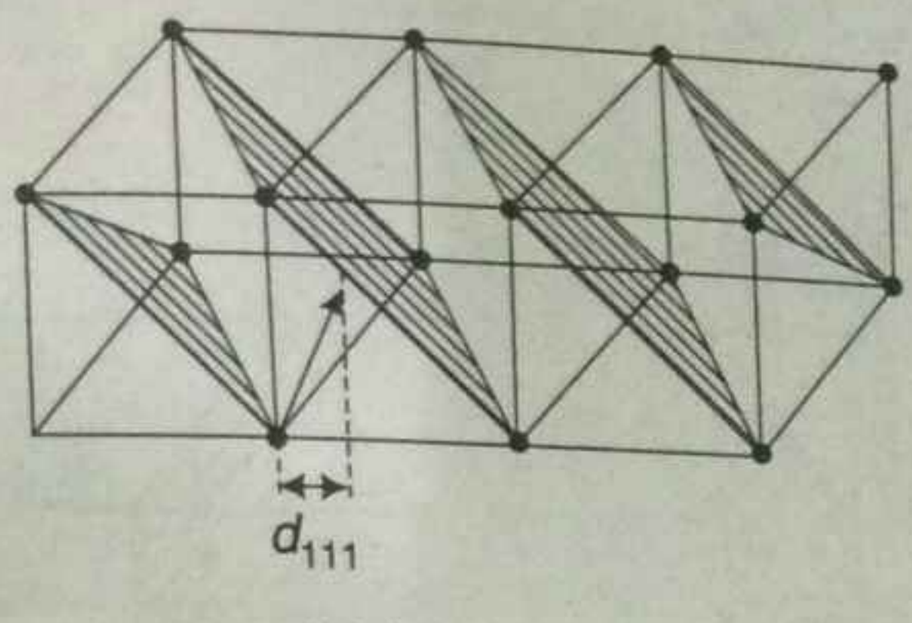
They are shown in Fig. 1.3.



(a) (100) Planes

(b) (110) Planes

Cond...



(c) (111) Planes

Fig. 1.3 Low index planes in simple cubic crystal: (a) (100) planes (b) (110) planes (c) (111) planes

Table 1.3 Interplanar spacings of various crystal systems

System	d_{hkl}
Cubic	$a(h^2 + k^2 + l^2)^{-1/2}$
Tetragonal	$\left[\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}\right]^{-1/2}$
Orthorhombic	$\left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right]^{-1/2}$
Hexagonal	$\left[\frac{4/3\,(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2}\right]^{-1/2}$
Rhombohedral	$\frac{a(1 + 2\cos 3\alpha - 3\cos^2\alpha)^{1/2}}{[(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + lh)(\cos^2\alpha - \cos\alpha)]^{1/2}}$
Monoclinic	$\left[\frac{h^2/a^2 + l^2/c^2 + (2hl\cos\beta)/ac}{\sin^2\beta} + \frac{k^2}{b^2}\right]^{-1/2}$
Triclinic	$\left[\frac{h}{a}\begin{vmatrix} h/a & \cos\gamma & \cos\beta \\ k/b & 1 & \cos\alpha \\ l/c & \cos\alpha & 1 \end{vmatrix} + \frac{k}{b}\begin{vmatrix} 1 & h/a & \cos\beta \\ \cos\gamma & k/b & \cos\alpha \\ \cos\beta & l/c & 1 \end{vmatrix} + \frac{1}{c}\begin{vmatrix} 1 & \cos\gamma & h/a \\ \cos\gamma & 1 & k/b \\ \cos\beta & \cos\alpha & l/c \end{vmatrix}\right]^{-1/2}$ $\Big/ \begin{vmatrix} 1 & \cos\gamma & \cos\beta \\ \cos\gamma & 1 & \cos\alpha \\ \cos\beta & \cos\alpha & 1 \end{vmatrix}^{-1/2}$

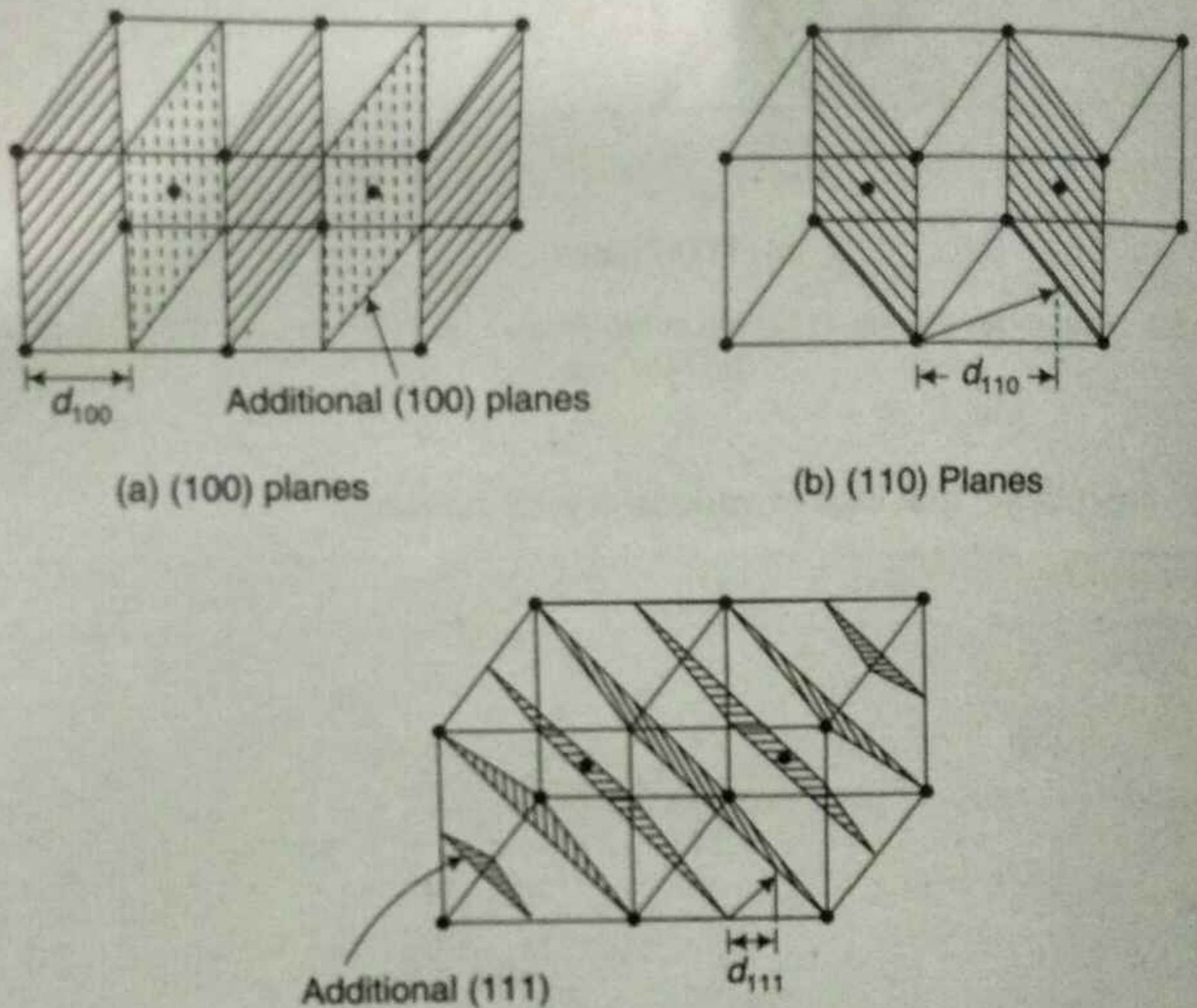
(b) Body centered cubic lattice

$$d_{100} = \frac{1}{2}(d_{100})\,sc = \frac{a}{2}$$

$$d_{110} = (d_{110})\,sc = \frac{a}{\sqrt{2}}$$

$$d_{111} = \frac{1}{2}(d_{111})sc = \frac{a}{2\sqrt{3}}$$

They are shown in Fig. 1.4.



(a) (100) planes

(b) (110) Planes

(c) (111) Planes

Fig. 1.4 Low index planes in *bcc* crystal: (a) (100) planes (b) (110) planes (c) (111) planes

(c) Face centered cubic lattice

$$d_{100} = \frac{1}{2}(d_{100})sc = \frac{a}{2}$$

$$d_{110} = \frac{1}{2}(d_{110})sc = \frac{a}{2\sqrt{2}}$$

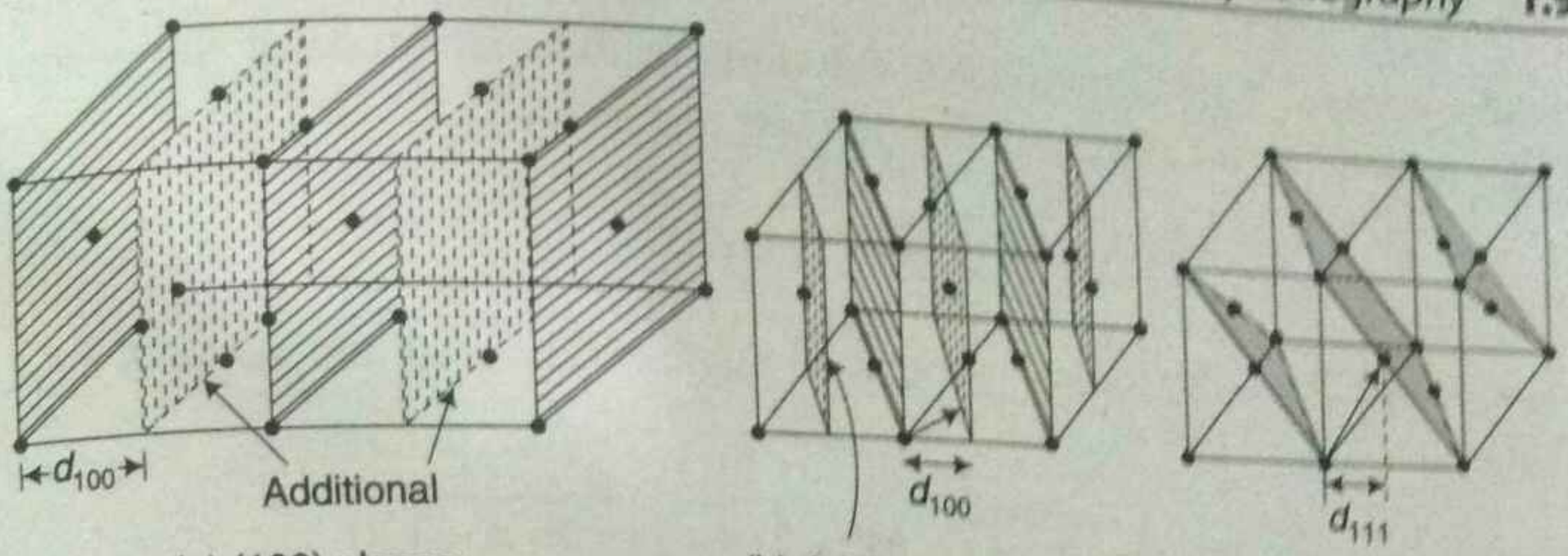
$$d_{111} = (d_{111})sc = \frac{a}{\sqrt{3}}$$

They are shown in Fig. 1.5.

1.8 SYMMETRY ELEMENTS IN CRYSTALLINE SOLIDS

Crystalline solids have following symmetry elements:

(i) Pure translation: $T = n_1 a + n_2 b + n_3 c$



(a) (100) planes (b) Additional (110) planes (c) (111) planes

Fig. 1.5 Low index planes in *fcc* crystal: (a) (100) (b) (110) plane (c) (111) planes

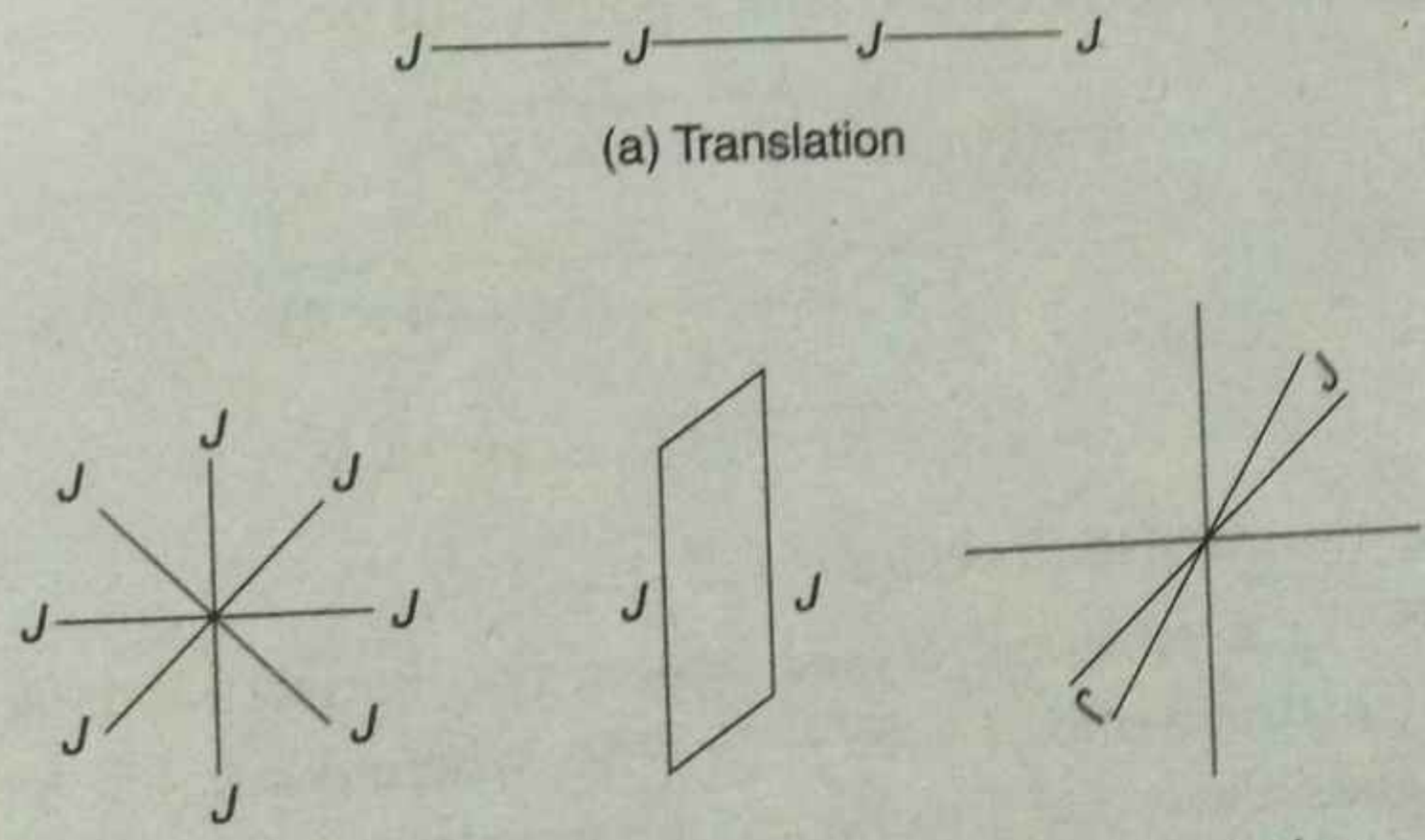
(ii) Proper rotation: $\phi = \frac{2\pi}{n}$, where $n = 1, 2, 3, 4$ and 6.

(iii) Reflection (mirror): m

(iv) Inversion center: $\bar{1}$

(v) Improper rotation: Rotoreflection/Rotoinversion

They are shown in Fig. 1.6.



(a) Translation (b) Rotation (c) Reflection (d) Inversion

Fig. 1.6 Simple symmetry operations

SOLVED EXAMPLES

Example 1.1 In a hexagonal plane lattice, the translation vector is given by $T = 2a + 3b$, where $a = b = 3$ Å and $\phi = 120°$. Determine the magnitude and direction of the translation vector.

Solution: Given: $a = b = 3$ Å, $\phi = 120°$, $n_1 = 2$, $n_2 = 3$. Direction of the translation vector T is [230].

Making use of the formula for determining the magnitude of the resultant vector as determined in a parallelogram law of forces, i.e.

$$R = \sqrt{P^2 + Q^2 + 2PQ\cos\phi}$$

where P and Q are the forces acting at an angle ϕ. The resultant vector R can be written as

$$R = \sqrt{(n_1 a)^2 + (n_2 b)^2 + 2(n_1 a)\,(n_2 b)\cos 120^\circ}$$

$$= \sqrt{(2\times 3)^2 + (3\times 3)^2 + 2(2\times 3)\,(3\times 3)\times\left(\frac{-1}{2}\right)}$$

$$= \sqrt{36 + 81 - 54} \simeq 7.94\ \text{Å}$$

Example 1.2 In a simple orthorhombic crystal system two lattice points are connected through the translation vector $T = 2a + 3b + 4c$, where $a = 2$ Å, $b = 3$ Å, and $c = 4$ Å. Determine the magnitude and direction of the translation vector.

Solution: Given: $a = 2$ Å, $b = 3$ Å, $c = 4$ Å, $n_1 = 2$, $n_2 = 3$ and $n_3 = 4$ we known that in an orthorhombic case, $\alpha = \beta = \gamma = 90^\circ$ and $\cos 90^\circ = 0$, therefore the length of the resultant vector between two lattice points will be

$$R = \sqrt{(n_1 a)^2 + (n_2 b)^2 + (n_3 c)^2}$$

$$= \sqrt{(2\times 2)^2 + (3\times 3)^2 + (4\times 4)^2}$$

$$= \sqrt{16 + 81 + 256} \simeq 18.79\ \text{Å}$$

Direction of the translation vector is [234].

Example 1.3 In a tetragonal crystal system two lattice points are connected through the translation vector $T = 3a + 4b + 5c$, where $a = b = 2$ Å and $c = 3$ Å. Determine the magnitude and direction of the translation vector.

Solution: Given: $a = b = 2$ Å, $c = 3$Å, $n_1 = 3$, $n_2 = 4$ and $n_3 = 5$.

We know that in a tetragonal system $\alpha = \beta = \gamma = 90^\circ$ and $\cos 90^\circ = 0$, therefore the length of the resultant vector between the two lattice points will be

$$R = \sqrt{(n_1 a)^2 + (n_2 b)^2 + (n_3 c)^2}$$

$$= \sqrt{(3\times 2)^2 + (4\times 2)^2 + (3\times 5)^2}$$

$$= \sqrt{36 + 64 + 225} \simeq 18.03\ \text{Å}$$

Direction of the translation vector is [345].

Example 1.4 Determine the distance between any two lattice points in a simple hexagonal system with $a = b = 3$ Å and $c = 4$ Å. Further, the integers $n_1 = 4$ units, $n_2 = 3$ units and $n_3 = 1$ unit, respectively.

Solution: In a simple hexagonal system, we know that $\alpha = \beta = 90°$ and $\gamma = 120°$, the translation vector between the required points can be determined in two steps. First in the same plane, the length of the resultant (say) R_1 will be

$$R_1 = \sqrt{(n_1 a)^2 + (n_2 b)^2 + 2(n_1 a)\,(n_2 b)\cos 120°}$$

$$= \sqrt{(4 \times 3)^2 + (3 \times 3)^2 + 2(4 \times 3)\,(3 \times 3)\left(\frac{-1}{2}\right)}$$

$$= \sqrt{144 + 81 - 108}$$

$$= \sqrt{117}$$

For Second step, $\cos 90° = 0$, therefore the resultant vector (say) R_2 will be

$$R_2 = \sqrt{117 + (n_3 c)^2}$$

$$= \sqrt{117 + (1 \times 4)^2}$$

$$= \sqrt{121} \simeq 11 \text{ Å}$$

Example 1.5 Draw Wigner-Seitz unit cells for the following lattices: (i) An oblique lattice in two dimensions, (ii) a bcc lattice and (iii) an *fcc* lattice in three dimensions.

Solution:

(i) Consider an oblique lattice (Fig. 1.7a). Take the central point as the reference point and proceed according to the given guidelines. Mark the mid-point of each line (Fig. 1.7b). Draw new lines through there midpoints. Join the new lines with each other to get the required Wigner-Seitz each other to get the required Wigner-Seitz unit cell (an irregular hexagon, Fig. 1.7c).

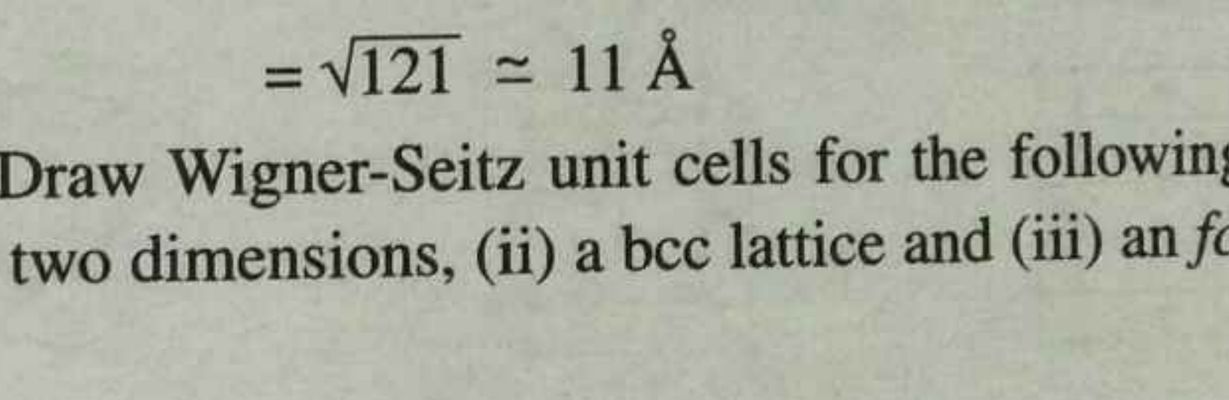
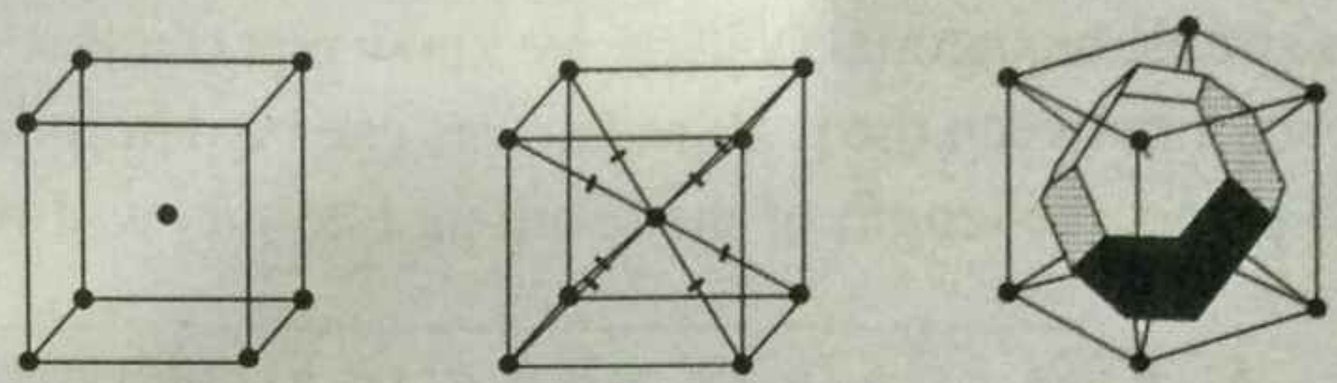


Fig. 1.7 Construction of Wigner-Seitz unit cell in two dimensions

(ii) Draw a normal bcc unit cell and consider the central point as the reference point (Fig. 1.8a). Connect this point with all other neighbouring points.

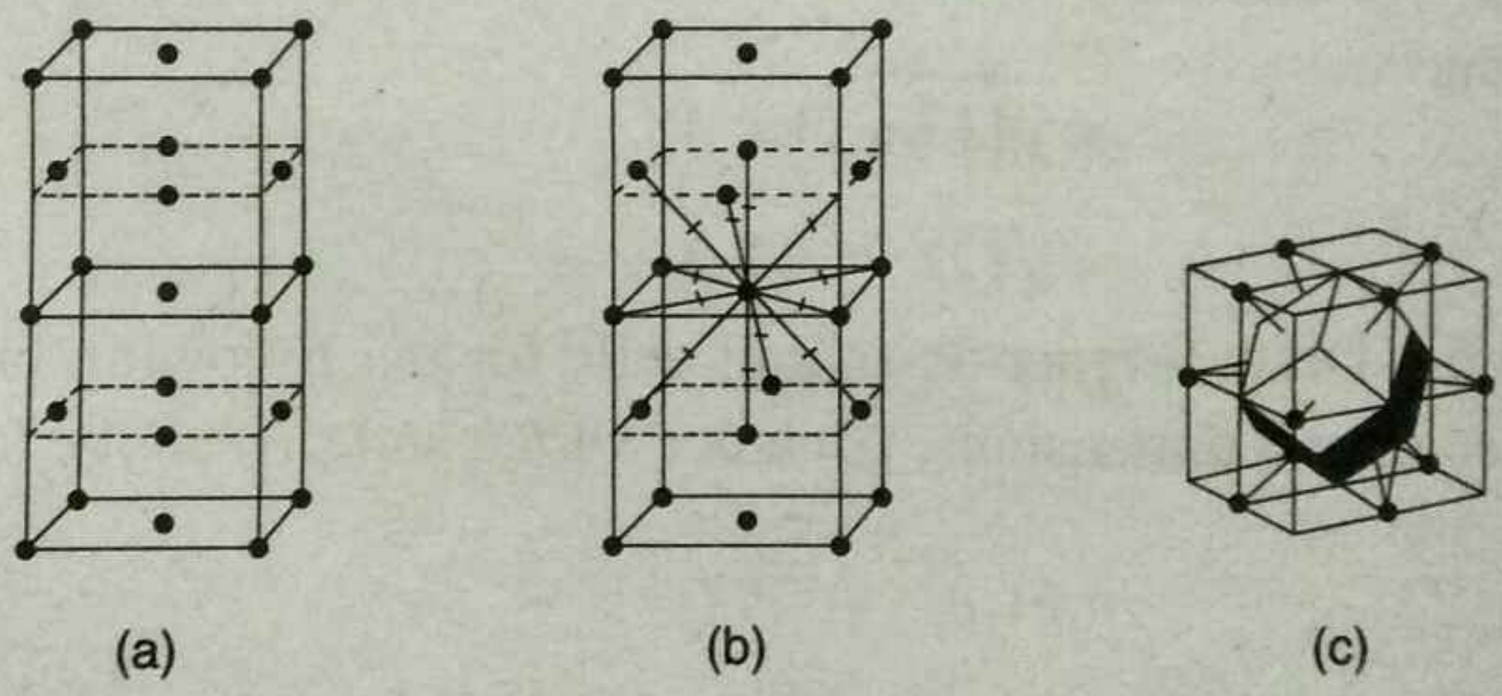
Mark midpoints on three lines (Fig. 1.8b). Draw planes through these midpoints. Volume enclosed by the intersection of these planes (a truncated octahedron) is the required Wigner-Seitz unit cell (Fig. 1.8c).



(a) (b) (c)

Fig. 1.8 Wigner-Seitz unit cell in a *bcc* unit

(iii) Draw two *fcc* unit cells one above the other. Select the reference point as shown in Fig. 1.9a. Connect this point with all other neighbouring points. Mark the midpoints on these lines (Fig. 1.9b). Draw planes through these midpoints. Volume enclosed by the intersection of these planes (a rhombic dodecahedron) is the required Wigner-Seitz unit cell (Fig. 1.9c).



(a) (b) (c)

Fig. 1.9 Wigner-Seitz unit cell in *fcc* unit

Example 1.6 A metallic element exists in the form of a cubic lattice. Each edge of the unit cell is 2.88 Å. The density of the metal is 7.2×10^3 kg/m^3. How many unit cells are there in 100 gm of the metal?

Solution: Given: Side of the unit cell $a = 2.88$ Å $= 2.88 \times 10^{-10}$ m, $\rho = 7.2 \times 10^3$ kg/m^3, mass of the metal = 100 gm = 0.1 kg, No. of unit cells = ?

Since the side of the cube $a = 2.88$ Å $= 2.88 \times 10^{-10}$ m, therefore, volume of the unit cell, $a^3 = (2.88 \times 10^{-10})^3$ m^3

$$= 23.9 \times 10^{-30} \text{ m}^3$$

We known that vol. of 0.1 kg metal $= \dfrac{\text{Mass}}{\text{Density}}$

$$= \frac{0.1}{7.2 \times 10^3} = 13.9 \times 10^{-6} \text{ m}^3$$

Further, No. of unit cells in 100 gm $= \dfrac{\text{Volume of 0.1 kg}}{\text{Volume of one unit cell}}$

$$= \frac{13.9 \times 10^{-6}}{23.9 \times 10^{-30}}$$

$= 5.82 \times 10^{23}$ unit cells.

Example 1.7 An element crystallizes into a cubic structure whose unit cell has one atom on each corner and two atoms on its face diagonals. If the volume of the cell is 24×10^{-30} m^3 and the density of the element is 7200 kg/m calculate the number of atoms present in 200 gm of the element.

Solution: Given: Mass of the element m = 200 gm = 0.2 kg, ρ = 7200 kg/m^3, vol. of the unit cell = 24×10^{-30} m^3, No. of atoms = ?

We know that vol. of 0.2 kg of element $= \dfrac{\text{Mass}}{\text{Density}}$

$$= \frac{0.2}{7200} = 2.78 \times 10^{-5} \text{ m}$$

Further, No. of unit cells in 0.2 kg of element

$$= \frac{\text{Vol. of 0.2 kg element}}{\text{Vol. of the unit cell}}$$

$$= \frac{2.78 \times 10^{-5}}{24 \times 10^{-30}}$$

$= 11.58 \times 10^{23}$ unit cells.

Now, the number of atoms per unit cell

$$= \left[\frac{1}{8} \times 8\right] + 2 = 3 \text{ atoms}$$

Therefore, number of atoms in 0.2 kg of materials

= (No. of atoms/unit cell) × No. of unit cells

$= 3 \times 11.58 \times 10^{23} = 34.75 \times 10^{23}$ atoms

Example 1.8 An element whose atomic mass is 100 has a bcc structure. Its unit cell parameter is 4 Å, calculate the density of the element, the number of unit cells and the number of atoms in 10 gm of the element.

Solution: Given: $M = 100$, structure *bcc*, so that $n = 2$, $a = 4\ \text{Å} = 4 \times 10^{-10}$ m, mass = 10 gm = 0.01 kg, ρ = ? No. of unit cells = ? No. of atoms = ?

We know that the density of the crystal material is given by

$$\rho = \frac{n \times M}{N \times a^3} = \frac{2 \times 100}{6.023 \times 10^{26} \times (4 \times 10^{-10})^3}$$

$$= 5188\ \text{kg/m}^3$$

Now, the vol. of 10 gm element $= \dfrac{\text{Mass}}{\text{Density}}$

$$= \frac{0.01}{5188} = 1.927 \times 10^{-6}\ \text{m}^3.$$

Therefore, No. of unit cells in 10 gm. element

$$= \frac{\text{Vol. of 10 gm element}}{\text{Vol. of the unit cell}}$$

$$= \frac{1.927 \times 10^{-6}}{64 \times 10^{-30}} = 3 \times 10^{22}\ \text{unit cells}$$

Further, the number of atoms in 10 gm of materials

= (No. of atoms/unit cell) × No. of unit cells

$$= 2 \times 3 \times 10^{22}$$

$$= 6 \times 10^{22}\ \text{atoms}$$

Example 1.9 An element crystallizes into *fcc* structure with its unit cell parameter as 2 Å. Calculate its density if 0.2 kg of the element contains 24×10^{23} atoms.

Solution: Given: Structure-*fcc*, so that $n = 4$, $a = 2\ \text{Å} = 2 \times 10^{-10}$ m, mass = 0.2 kg, No. of atoms (in 0.2 kg) $= 24 \times 10^{23}$, ρ = ?

We know that the total number of atoms is

= (Atoms/unit cell) × No. of unit cells

$$\Rightarrow \quad \text{No. of unit cells} = \frac{\text{Total number of atoms}}{\text{Atoms/unit cell}}$$

$$= \frac{24 \times 10^3}{4} = 6 \times 10^{23}$$

Further, Volume of the substance

= No. of unit cells × Vol. of the unit cell

$$= 6 \times 10^{23} \times (2 \times 10^{-10})^3$$

$$= 48 \times 10^{-7}\ \text{m}^3.$$

Now, the density of the crystal material is given by

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{0.2}{48 \times 10^{-7}} = 4.17 \times 10^4\ \text{kg/m}^3$$

Example 1.10 An element crystallizes into *fcc* structure. 208 gms. of the substance contain 4.28×10^{24} atoms. Calculate the length of the unit cell if its density is 7200 kg/m^3.

Solution: Given: Crystal structure-*fcc*, so that $n = 4$, mass of the substance = 208 gms. = 0.208 kg, No. of atoms = 4.28×10^{24}, $\rho = 7200$ kg/m^3, $a = ?$

We know that the No. of atoms in 0.208 kg of materials are = (No. of atoms/unit cell) × No. of unit cells

or $$4.28 \times 10^{24} = 4 \times \text{No. of unit cells}$$

or $$\text{No. of unit cells} = \frac{4.28 \times 10^{24}}{4} = 1.07 \times 10^{24}$$

Further, Vol. of 0.208 kg of materials is

$$\text{Volume} = \frac{\text{Mass}}{\text{Density}} = \frac{0.208}{7200} = 2.89 \times 10^{-5}$$

$$\text{Therefore, Vol. of the unit cell } (a^3) = \frac{\text{Vol. of 0.208 kg of materials}}{\text{No. of unit cells in 0.208 kg}}$$

$$= \frac{2.89 \times 10^{-5}}{1.07 \times 10^{24}} = 27.00 \times 10^{-30}$$

$$\Rightarrow \quad a = (27 \times 10^{-30})^{1/3}$$

$$= 3 \times 10^{-10}\ \text{m} = 3\ \text{Å}$$

Example 1.11 A unit cell of NaCl has four formula units. Calculate its density if the side of the unit cell is 5.64 Å.

Solution: Given: $n = 4$, $a = 5.64$ Å $= 5.64 \times 10^{-10}$ m, Mol. weight of NaCl = 23 + 35.5 = 58.5, $\rho = ?$

We know that the density of the crystal material is given by

$$\rho = \frac{\text{Mass}}{\text{Volume}} = \frac{n \times M}{N \times a^3} = \frac{4 \times 58.5}{6.023 \times 10^{26} \times (5.64 \times 10^{-10})^3}$$

$$= 2165\ \text{kg/m}^3$$

Example 1.12 Sodium chloride has *fcc* structure. Its density is 2.18×10^3 kg/m^3. The atomic weights of sodium and chlorine are 23 and 35.5, respectively. Calculate the interatomic separation.

Solution: Mol. weight of NaCl = 23 + 35.5 = 58.5, $\rho = 2.18 \times 10^3$ kg, structure is *fcc*, so that $n = 4$, $a = ?$, $d = \left(\frac{a}{2}\right) = ?$

We know that the density of the crystal material is given by

$$\rho = \frac{\text{Mass}}{\text{Volume}} = \frac{n \times M}{N \times a^3}$$

where a is the side of the unit cell.

$$\Rightarrow \quad a^3 = \frac{n \times M}{N \times \rho} \quad \text{or} \quad a = \left(\frac{n \times M}{N \times \rho}\right)^{1/3}$$

$$= \left(\frac{4 \times 58.5}{6.023 \times 10^{26} \times 2.18 \times 10^3}\right)^{1/3}$$

$$= 5.63 \times 10^{-10} \text{ m}$$

Therefore, the interatomic distance

$$d = \frac{a}{2} = \frac{5.63 \times 10^{-10}}{2}$$

$$= 2.81 \times 10^{-10} \text{ m.}$$

Example 1.13 Potassium chloride crystal has a density of 1.98×10^3 kg/m^3 and its molecular weight is 74.55. Find the interatomic distance.

Solution: Given: Since KCl has NaCl structure, so that $n = 4$, $\rho = 1.98 \times 10^3$ kg/m^3, $M = 74.55$, $a = ?$, $d = \left(\frac{a}{2}\right) = ?$

We know that the density of the crystal material is given by

$$\rho = \frac{\text{Mass}}{\text{Volume}} = \frac{n \times M}{N \times a^3},$$

where a is the side of the unit cell.

$$\text{or} \quad a^3 = \frac{n \times M}{N \times \rho} \quad \text{or} \quad a = \left(\frac{n \times M}{N \times \rho}\right)^{1/3}$$

$$= \left(\frac{4 \times 74.55}{6.023 \times 10^{26} \times 1.98 \times 10^3}\right)^{1/3}$$

$$= 6.30 \times 10^{-10} \text{ m}$$

Therefore,

$$d = \frac{a}{2} = \frac{6.30 \times 10^{-10}}{2}$$

$$= 3.15 \times 10^{-10} \text{ m.}$$

Example 1.14 The nearest neighbour distance in a silver crystal is 2.87 Å. Silver crystallizes in *fcc* form, determine its density.

Solution: Given: Crystal structure is *fcc*, so that $n = 4$, Nearest neighbour distance = 2.87 Å = 2.87×10^{-10} m, At. wt. of silver = 107.68, $\rho = ?$

We know that the nearest neighbour distance in *fcc* crystal is $a/\sqrt{2}$

$$\Rightarrow \qquad \frac{a}{\sqrt{2}} = 2.87 \times 10^{-10} \quad \text{or} \quad a = \sqrt{2} \times 2.87 \times 10^{-10}$$

$$= 4.06 \times 10^{-10} \text{ m.}$$

Now the density of crystal material is given by

$$\rho = \frac{\text{Mass}}{\text{Volume}} = \frac{n \times M}{N \times a^3}$$

$$= \frac{4 \times 107.68}{6.023 \times 10^{26} \times (4.06 \times 10^{-10})^3}$$

$$= 1.068 \times 10^4 \text{ kg/m}^3.$$

Example 1.15 Aluminium has *fcc* structure and iron has bcc structure. The densities of aluminum and iron are 2.70×10^3 and 7.87×10^3 kg/m^3, respectively. The lattice parameter of *Al* is 4.04 Å and that of *Fe* is 2.86 Å. Determine the atomic mass of these elements.

Solution: Given: (i) Structure (*Al*)-*fcc*, so that $n = 4$, $\rho(Al) = 2.7 \times 10^3$ kg/m^3, $a(Al) = 4.04$ Å $= 4.04 \times 10^{-10}$ m, $M(Al) = ?$

(ii) Structure (*Fe*)-*bcc*, so that $n = 2$, $\rho(Fe) = 7.87 \times 10^3$ kg/m^3, $a(Fe) = 2.86$ Å $= 2.86 \times 10^{-10}$ m, $M(Fe) = ?$

We know that the density of the crystal material is given by

$$\rho = \frac{\text{Mass}}{\text{Volume}} = \frac{n \times M}{N \times a^3}$$

or $$M = \frac{N \times a^3 \times \rho}{n},$$ Therefore,

$$M(Al) = \frac{6.023 \times 10^{26} \times (4.04 \times 10^{-10})^3 \times 2.7 \times 10^3}{4}$$

$$= 26.81$$

Similarly,

$$M(Fe) = \frac{6.023 \times 10^{26} \times (2.86 \times 10^{-10})^3 \times 7.87 \times 10^3}{2}$$

$$= 55.44$$

Example 1.16 Calculate the radius of atom in α-iron belonging to a *bcc* structure. The density of α-iron is 7860 kg/m^3 and the atomic weight is 55.85.

Solution: Given: $\rho = 7860$ kg/m^3, at.wt. = 55.85, structure is *bcc*, so that $n = 2$, $r = ?$

We know that the density of crystal material is given by

$$\rho = \frac{\text{Mass}}{\text{Volume}} = \frac{n \times M}{N \times a^3} \quad \text{or} \quad a^3 = \frac{n \times M}{N \times \rho}$$

or

$$a = \left(\frac{n \times M}{N \times \rho}\right)^{1/3} = \left(\frac{2 \times 55.85}{6.023 \times 10^{26} \times 7860}\right)^{1/3}$$

$$= 2.86 \times 10^{-10} \text{ m} = 2.86 \text{ Å}$$

Further, in a bcc structure, we have

$$4r = \sqrt{3}a$$

where r is the radius of the atom. Therefore,

$$r = \frac{\sqrt{3} \times 2.86}{4} = 1.24 \text{ Å}$$

Example 1.17 Zinc has *hcp* structure. The height of the unit cell is 4.94 Å, the nearest neighbour distance is 2.7 Å and the atomic weight of zinc is 65.38. Calculate the density of zinc.

Solution: Given: $a = b = 2.7$ Å $= 2.7 \times 10^{-10}$ m, $c = 4.94$ Å $= 4.94 \times 10^{-10}$ m at.wt. of $Zn = 65.37$, structure is *hcp*, so that $n = 6$, $\rho = ?$

We know that the volume of the *hcp* cell is given by

$$V = \frac{3\sqrt{3}a^2c}{2}$$

$$= \frac{3 \times 1.732 \times (2.7 \times 10^{-10})^2 \times 4.94 \times 10^{-10}}{2}$$

$$= 93.56 \times 10^{-30} \text{ m}^3.$$

Now the density of the crystal material is obtained by $\rho = \frac{n \times M}{N \times V}$

$$= \frac{6 \times 65.38}{6.023 \times 10^{26} \times 93.56 \times 10^{-30}}$$

$$= 6961 \text{ kg/m}^3$$

Example 1.18 Calculate the density of points (atoms) in (100), (110) and (111) planes of a simple cubic structure whose lattice parameter is 2.5 Å.

Solution: Given: Crystal planes – (100) (110) and (111), crystal structure is *Sc* so that $n = 1$, $a = 2.5$ Å $= 2.5 \times 10^{-1}$ $\rho = ?$

We know that the density of atoms in a crystal plan is given by

$$\rho_p = \frac{\text{No. of atoms in the given plane}}{\text{Area of the given plane}} = \frac{n'}{A} = \frac{nd}{V}$$

For simple cubic structure, we know that

$$d_{100} = 1, d_{110} = \frac{a}{\sqrt{2}} \quad \text{and} \quad d_{111} = \frac{a}{\sqrt{3}}, V = a^3$$

$$\text{Therefore, } \rho_{(100)} = \frac{1 \times d_{100}}{a^3} = \frac{1 \times a}{a^3} = \frac{1}{a^2}$$

$$= \frac{1}{(2.5 \times 10^{-10})^2}$$

$$= 9.2 \times 10^{18} \text{ atoms/m}^2$$

Example 1.19 Calculate the density of points (atoms) in (100), (110) and (111) planes of *bcc* iron whose lattice parameter is 2.87 Å.

Solution: Given: Crystal planes – (100), (110) and (111), crystal structure is *bcc*, so that $n = 2$, $a = 2.87$ Å $= 2.87 \times 10^{-10}$ m, $\rho = ?$

We know that the density of atoms in a crystal plane is given by

$$\rho_p = \frac{nd}{V}$$

For *bcc* structure, we know that

$$d_{100} = \frac{a}{2}, d_{110} = \frac{a}{\sqrt{2}} \quad \text{and} \quad d_{111} = \frac{a}{2\sqrt{3}}, V = a^3$$

$$\text{Therefore, } \rho_{(100)} = \frac{2 \times d_{100}}{a^3} = \frac{2a}{2a^3} = \frac{1}{a^2}$$

$$= \frac{1}{(2.87 \times 10^{-10})^2} = 1.21 \times 10^{19} \text{ atoms/m}^2$$

$$\text{Similarly, } \rho_{(110)} = \frac{2 \times d_{110}}{a^3} = \frac{2a}{\sqrt{2}a^3} = \frac{\sqrt{2}}{a^2}$$

$$= \frac{\sqrt{2}}{(2.87 \times 10^{-10})^2}$$

$$= 1.72 \times 10^{19} \text{ atoms/m}^2$$

and $$\rho_{(111)} = \frac{2 \times d_{111}}{a^3} = \frac{2a}{2\sqrt{3}a^3} = \frac{1}{\sqrt{3}a^2}$$

$$= \frac{1}{\sqrt{3} \times (2.87 \times 10^{-10})^2}$$

$$= 7 \times 10^{18} \text{ atoms/m}^2$$

Example 1.20 Calculate the density of atoms in (100), (110) and (111) planes of *fcc* aluminum whose lattice parameter is 4.05 Å.

Solution: Given: Crystal planes – (100), (110) and (111), crystal structure is *fcc*, so that $n = 4$, $a = 4.05$ Å $= 4.05 \times 10^{-10}$ m, $\rho = ?$

We know that the density of atoms in a crystal plane is given by

$$\rho_p = \frac{nd}{V}$$

For *fcc* structure, we know that

$$d_{100} = \frac{a}{2}, d_{110} = \frac{a}{2\sqrt{2}} \quad \text{and} \quad d_{111} = \frac{a}{\sqrt{3}}, V = a^3$$

Therefore, $$\rho_{(100)} = \frac{4 \times d_{100}}{a^3} = \frac{4a}{2a^3} = \frac{2}{a^2}$$

$$= \frac{2}{(4.05 \times 10^{-10})^2}$$

$$= 1.22 \times 10^{19} \text{ atoms/m}^2$$

Similarly,

$$\rho_{(110)} = \frac{4 \times d_{110}}{a^3} = \frac{4a}{2\sqrt{2}a^3} = \frac{\sqrt{2}}{a^2}$$

$$= \frac{\sqrt{2}}{(4.05 \times 10^{-10})^2}$$

$$= 8.62 \times 10^{18} \text{ atoms/m}^2$$

and $$\rho_{(111)} = \frac{4 \times d_{111}}{a^3} = \frac{4a}{\sqrt{3}a^3} = \frac{4}{\sqrt{3}a^2}$$

$$= \frac{4}{\sqrt{3} \times (4.05 \times 10^{-10})^2}$$

$$= 1.41 \times 10^{19} \text{ atoms/m}^2$$

Example 1.21 Calculate the density of atoms in (0001) plane of *hcp* zinc, whose lattice parameters $a = b = 2.66$ Å and $c = 4.95$ Å.

Solution: Given: Crystal structure is hcp, crystal plane (0001), $a = b = 2.66$ Å $= 2.66 \times 10^{-10}$ m, $c = 4.95$ Å $= 4.95 \times 10^{-10}$ m, $\rho = ?$

We know that the density of atoms in a crystal plane is given by

$$\rho_p = \frac{\text{No. of atoms in the given plane}}{\text{Arca of the given plane}}$$

Here, the no. of atoms in the hcp basal plane (0001) $= \frac{1}{2}$ (one center atom is associated with two unit cells $+ 6 \times \frac{1}{6}$ (each of the six corner atom is surrounded by six unit cells)

$$= \frac{1}{2} + 1 = \frac{3}{2}$$

$$\text{Area of the hexagon} = \frac{3\sqrt{3}a^2}{2}$$

$$\text{Therefore, } \rho_{(0001)} = \frac{3/2}{\frac{3\sqrt{3}a^2}{2}} = \frac{1}{\sqrt{3}a^2}$$

$$= 8.16 \times 10^{18} \text{ atoms/m}^2$$

Example 1.22 Calculate the linear atomic density along [100], [110] and [111] directions in *bcc* iron whose lattice parameter is 2.87 Å.

Solution: Given: Crystal Structure is *bcc*, crystal directions are [100], [110] and [111], $a = 2.87$ Å $= 2.87 \times 10^{-10}$ m, $\rho = ?$

We know that the linear atomic density along a particular direction is given by

$$\rho_l = \frac{\text{No. of atoms intersected by the length of the line}}{\text{Length of the line}}$$

$$\text{Therefore, } \rho_{[100]} = \frac{1}{a}$$

$$= \frac{1}{2.87 \times 10^{-10}}$$

$$= 3.48 \times 10^9 \text{ atoms/m}$$

Similarly, $\rho_{[110]} = \frac{1}{\sqrt{2}a} = \frac{1}{\sqrt{2} \times (2.87 \times 10^{-10})}$

$= 2.46 \times 10^{9}$ atoms/m

and $\rho_{[111]} = \frac{2}{\sqrt{3}a} = \frac{2}{\sqrt{3} \times (2.87 \times 10^{-10})}$

$= 4.02 \times 10^{9}$ atoms/m

Example 1.23 Calculate the linear atomic density along [100], [110] and [111] directions in *fcc* copper whose lattice parameter is 3.61 Å.

Solution: Given: Crystal structure is *fcc*, crystal directions are [100], [110] and [111], $a = 3.61$ Å $= 3.61 \times 10^{-10}$ m, $\rho = ?$

We know that the linear atomic density along a particular direction is given by

$$\rho_l = \frac{\text{No. of atoms intersected by the length of the line}}{\text{Length of the line}}$$

Therefore, $\rho_{[100]} = \frac{1}{a} = \frac{1}{3.61 \times 10^{-10}}$

$= 2.77 \times 10^{9}$ atoms/m

Similarly, $\rho_{[110]} = \frac{2}{\sqrt{2}a} = \frac{\sqrt{2}}{a}$

$= \frac{\sqrt{2}}{3.61 \times 10^{-10}}$

$= 3.92 \times 10^{9}$ atoms/m

and $\rho_{[111]} = \frac{1}{\sqrt{3}a} = \frac{1}{3.61 \times 10^{-10}}$

$= 1.60 \times 10^{9}$ atoms/m

Example 1.24 How the atomic positions are located in cubic unit cells? Find the position coordinates for the atoms in *bcc* and *fcc* unit cells.

Solution: Following the instructions given above, the atomic positions can be located in cubic unit cells in terms of unit distances along x, y and z-axes as shown in Fig. 1.1. For simple cubic unit cell, they are:

[[000]], [[100]], [[010]], [[001]]
[[110]], [[101]], [[011]], [[111]]

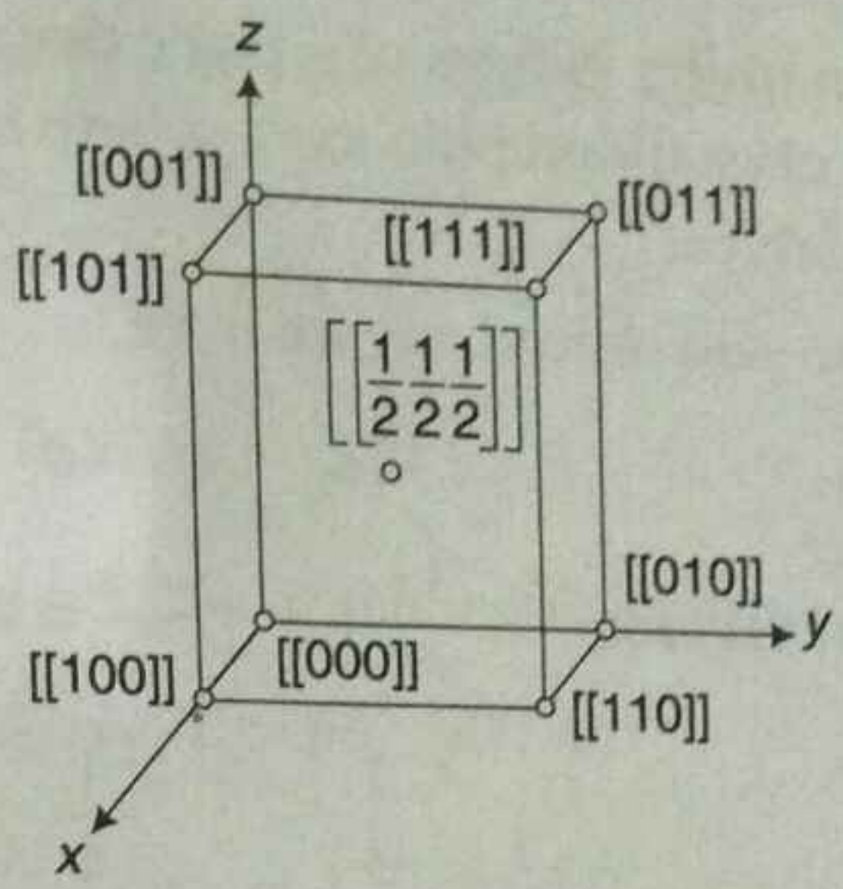


Fig. 1.10 The position coordination of the central atom and corner ate in a *bcc* unit cell

The position coordinates for the eight corner atoms of the *bcc* unit cell remain the same as for simple cubic case. The position coordinated of the central atom in a *bcc* unit cell are $\left[\left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\right]\right]$ as shown in Fig. 1.10. For simplicity sometimes only two position coordinates, e.g. [[000]] and $\left[\left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\right]\right]$ are specified to represent a *bcc* unit cell while other position coordinates (corner atoms) are assumed to be understood.

Atomic positions in an *fcc* unit cell are shown in Fig. 1.11. The position coordinates for the eight corner atoms remain the same as for *sc* or *bcc* unit cell. The position coordinates of the six face centered atoms are: $\left[\left[\frac{1}{2}\frac{1}{2}0\right]\right]$, $\left[\left[0\frac{1}{2}\frac{1}{2}\right]\right]$, $\left[\left[\frac{1}{2}0\frac{1}{2}\right]\right]$, $\left[\left[\frac{1}{2}\frac{1}{2}1\right]\right]$, $\left[\left[1\frac{1}{2}\frac{1}{2}\right]\right]$ and $\left[\left[\frac{1}{2}1\frac{1}{2}\right]\right]$.

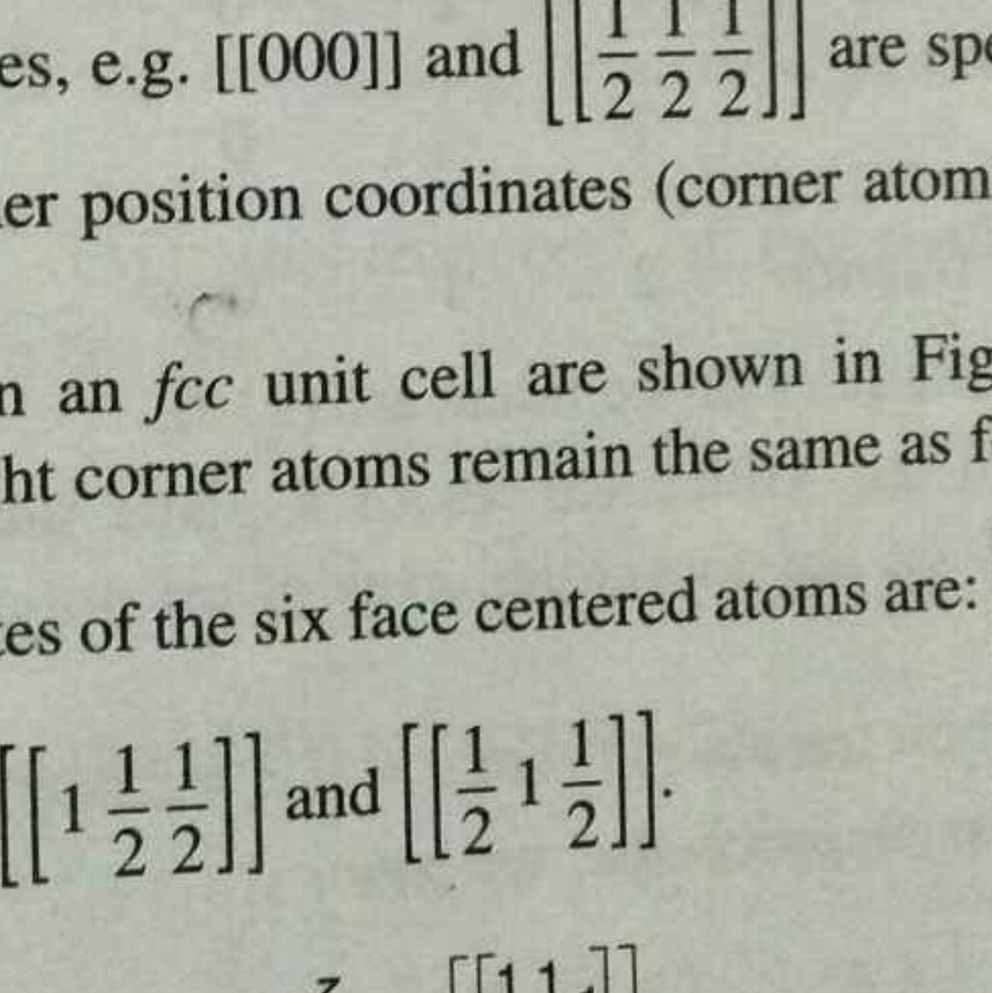


Fig. 1.11 The position coordinates of face centered atoms in an *fcc* unit cell

Example 1.25 Find the Miller indices of a plane that makes an intercept of $3a$, $4b$ and $6c$ along the there crystallographic axes, where a, b, c being the primitive translation vectors of the lattice.

Solution: Following the said procedure, we have

(i) Intercepts	$3a$	$4b$	$6c$
(ii) Division by unit translation	$\frac{3a}{a}=3$	$\frac{4b}{b}=4$	$\frac{6c}{c}=6$
(iii) Reciprocals	$\frac{1}{3}$	$\frac{1}{4}$	$\frac{1}{6}$
(iv) After clearing fraction	4	3	2

$\Rightarrow$ The required Miller indices of the plane are (432).

Example 1.26 Find the Miller indices of a plane that makes an intercept of 1 on a-axis, 2 on b-axis and is parallel to the c-axis.

Solution: Following the said procedure, we have

(i) Intercepts	1	2	0
(ii) Reciprocals	1	$\frac{1}{2}$	0
(iii) After clearing fraction	2	1	0

$\Rightarrow$ The required Miller indices of the plane are (210).

Example 1.27 Find the Miller indices of a plane that makes an intercept of 3 Å, 4 Å, and 5 Å on the coordinate axes of an orthorhombic crystal with $a: b: c = 1: 2: 5$.

Solution: Here the unit translations are $a = 1$, $b = 2$ and $c = 5$

Now following the same procedure, we have

(i) Intercepts	3	4	5
(ii) Division by unit translation	$\frac{3}{1}=3$	$\frac{4}{2}=2$	$\frac{5}{5}=1$
(iii) Reciprocals	$\frac{1}{3}$	$\frac{1}{2}$	1
(iv) After clearing fraction	2	3	6

$\Rightarrow$ The required Miller indices of the plane are (236).

Example 1.28 In an orthorhombic cell, the primitive vectors are 1.27 Å, 2.14 Å and 1.51 Å. Deduce the intercepts of x and y axes if (213) plane cuts an intercept of 1.51 Å along the z-axis.

Solution: We known that reciprocal of the coefficients of unit translation vectors are in the ratio:

$$p^{-1} : q^{-1} : r^{-1} = h : k : l = 2 : 1 : 3$$

Therefore, $$p : q : r = \frac{1}{2} : 1 : \frac{1}{3}$$

Then the ratio of actual lengths of the intercepts are

$$l_1 : l_2 : l_3 = pa : qb : rc$$

$$= 1.27 \times \frac{1}{2} : 2 \cdot 14 \times 1 : 1.51 \times \frac{1}{3}$$

Since l_3 is given as 1.51 Å, we therefore multiply the R.H.S by 3, so that

$$l_1 : l_2 : l_3 = 1.90 : 6.42 : 1.51$$

$\Rightarrow$ $$l_1 = 1.90 \text{ Å} \quad \text{and} \quad l_2 = 6.242 \text{ Å}.$$

Example 1.29 Find the lengths of the intercepts made by the planes of Miller indices (111) and (123) in $BaCl_2$ crystal with primitive translation vectors $a = 6.69$ Å, $b = 10.86$ Å and $c = 7.15$ Å, if both the planes cut an intercept of 7.15 Å along the z-axis.

Solution: For plane (111), the reciprocal of the coefficients of the unit translation vectors are in the ratio:

$$p^{-1} : q^{-1} : r^{-1} = h : k : l = 1 : 1 : 1$$

Therefore $p : q : r = 1 : 1 : 1$

The ratio of actual lengths of the intercepts are

$$l_1 : l_2 : l_3 = pa : qb : rc$$

$$= 6.69 \times 1 : 10.86 \times 1 : 7.15 \times 1$$

$$= 6.69 : 10.86 : 7.15$$

$\Rightarrow$ $$l_1 = 6.69 \text{ Å}, l_2 = 10.86 \text{ Å} \quad \text{and} \quad l_3 = 7.15 \text{ Å}.$$

Similarly, for plane (123), we have

$$p^{-1} : q^{-1} : r^{-1} = h : k : l = 1 : 2 : 3$$

Therefore $p : q : r = 1 : \frac{1}{2} : \frac{1}{3}$

The ratio of actual lengths of the intercepts are

$$l_1 : l_2 : l_3 = pa : qb : rc$$

$$= 6.69 \times 1 : 10.86 \times 1/2 : 7.15 \times \frac{1}{3}$$

Since l_3 is given as 7.15 Å, we therefore multiply the R.H.S by 3 so that

$$l_1 : l_2 : l_3 = 20.07 : 16.29 : 7.15$$

$$\Rightarrow \qquad l_1 = 20.07 \text{ Å}, \; l_2 = 16.29 \text{ Å} \quad \text{and} \quad l_3 = 7.15 \text{ Å}.$$

Example 1.30 $\left[\left[\frac{a}{2}\, b\, 0\right]\right]$ are the coordinates of the lattice site nearest to the origin. Find the indices of direction.

Solution: Following the said procedure, we have

(i) Coordinates	$\frac{a}{2}$	b	0
(ii) Division by unit translation	$\frac{a}{2a} = \frac{1}{2}$	$\frac{b}{b} = 1$	$\frac{0}{c} = 0$
(iii) After clearing fraction	1	2	0

$\Rightarrow$ The required indices of directions are [120].

Example 1.31 The coordinates of a lattice site nearest to the origin is given by $x = -2a$, $y = 1b$ and $z = \frac{3c}{2}$. Determine the indices of direction.

Solution: Following the said procedure, we have

(i) Coordinates	$-2a$	$1b$	$\frac{3}{2}c$
(ii) Division by unit translation	$\frac{-2a}{a} = -2$	$\frac{1b}{b} = 1$	$\frac{3c}{2c} = \frac{3}{2}$
(iii) After clearing fraction	-4	2	3

$\Rightarrow$ The required indices of direction are $[\bar{4}\ 2\ 3]$.

Example 1.32 The coordinates of two sites of a cubic lattice are given by [[110]] and [[011]], respectively. Calculate the angle between them.

Solution: Given: Two lattice sites – [[110]] and [[011]], $\theta = ?$

Since the given lattice sites do not have fractional numbers in them and being smallest digit, they will represent the directions as well. Therefore, the two directions are: [110] and [011]. In fact, they are different diagonals of a cube.

Now, making use of the formula given in Table 1.2, we obtain

$$\cos\theta = \frac{0 + 1 + 0}{\sqrt{2} \times \sqrt{2}} = \frac{1}{2}$$

$$\Rightarrow \qquad \theta = 60°.$$

Example 1.33 Write all the members of the family of directions <100>, <110> and <111> in a cubic system.

Solution: The family <100> comprises of six crystallographically equivalent directions. They are: [100], $[\bar{1}00]$, [010], $[0\bar{1}0]$, [001] and $[00\bar{1}]$.

Similarly, the family <110> comprises of twelve crystallographically equivalent directions. They are: [110], $[\bar{1}10]$, $[1\bar{1}0]$, $[\bar{1}\,\bar{1}0]$, [101], $[\bar{1}01]$, $[10\bar{1}]$, $[\bar{1}0\bar{1}]$, [011], $[0\bar{1}1]$, $[01\bar{1}]$ and $[0\bar{1}\,\bar{1}]$. Also the family <111> comprises of eight crystallographically equivalent directions. They are: [111], $[\bar{1}11]$, $[1\bar{1}1]$, $[11\bar{1}]$, $[\bar{1}\,\bar{1}1]$, $[1\bar{1}\,\bar{1}]$ and $[\bar{1}\,\bar{1}\,\bar{1}]$.

Example 1.34 Classify the members of the family of directions <100>, <110> and <111> in a tetragonal system.

Solution: For a tetragonal system, we know that $a = b \neq c$. Thus, the unit translations for the directions [100], $[\bar{1}00]$, [010], and $[0\bar{1}0]$ is the same as a, whereas for the directions [001] and $[00\bar{1}]$ is c. Accordingly, the initial four directions are the members of <100> family and the last two are the members of <001> family.

In a cube, the twelve directions (face diagonals) lie in three different planes (viz. x-y, y-z and z-x) but they are crystallographically equivalent because $a = b = c$. Unlike this, in tetragonal ($a = b \neq c$) all twelve directions are not equivalent. For x-y plane $a = b$ and the corresponding unit translation is $\sqrt{2}a$ Table 1.4. The y-z and z-x planes have the unit translation is $\sqrt{a^2 + c^2}$. Accordingly, <110> family has four members. They are: [110], $[\bar{1}10]$, $[1\bar{1}0]$ and $[\bar{1}\,\bar{1}0]$. On the other hand, eight directions [101], $[\bar{1}01]$, $[10\bar{1}]$, $[\bar{1}0\bar{1}]$, [011], $[0\bar{1}1]$, $[01\bar{1}]$ and $[0\bar{1}\,\bar{1}]$ are the members of <101> family or equivalently the <011> family.

Table 1.4 The unit translation for low index directions of a tetragonal system

Family	Unit translation	
	P	*I*
<100>	a	a
<001>	c	c
<110>	$\sqrt{2}a$	$\sqrt{(a^2 + c^2)}$
<101>	$\sqrt{(a^2 + c^2)}$	$\frac{1}{2}\sqrt{(2a^2 + c^2)}$
<111>	$\sqrt{(2a^2 + c^2)}$	$\sqrt{2a^2 + c^2}$

Since all <111> directions have the same unit translation $\left(\sqrt{2a^2 + c^2}\right)$ in tetragonal system like cubic system, this family contains all eight members. They are: [111], $[\bar{1}11]$, $[1\bar{1}1]$, $[11\bar{1}]$, $[\bar{1}\,\bar{1}1]$, $[1\bar{1}\,\bar{1}]$ and $[\bar{1}\,\bar{1}\,\bar{1}]$.

Example 1.35 Classify the members of the family of directions <100>, <110> and <111> in an orthorhombic system.

Solution: For an orthorhombic system we know that $a \neq b \neq c$. Thus, the unit translation for the directions [100] and $[\bar{1}00]$ is a (Table 1.5), for [010] and $[0\bar{1}0]$ is b and for [001] and $[00\bar{1}]$ is c. Accordingly, the first two directions are the members of <100> family, the next two directions are the members of <010> family and the last two directions are the members of <001> family. Since $a \neq b \neq c$ in an orthorhombic system, the conditions for x-y, y-z and z-x planes are different. In other words, the unit translations along different planes are different. Accordingly, <110> family has four members. They are [110], $[\bar{1}10]$, $[1\bar{1}0]$ and $[\bar{1}\,\bar{1}0]$. Similarly, <101> family has other four members: [101], $[\bar{1}01]$, $[10\bar{1}]$ and $[\bar{1}0\bar{1}]$. Finally, <011> family has the remaining four members: [011], $[0\bar{1}1]$, $[01\bar{1}]$ and $[0\bar{1}\,\bar{1}]$.

Table 1.5 The unit translation for low index directions of an orthorhombic system

	Unit translation			
Family	*P*	*c*	*I*	*F*
<100>	a	a	a	a
<010>	b	b	b	b
<001>	c	c	c	c
<110>	$\sqrt{(a^2+b^2)}$	$\frac{1}{2}\sqrt{(a^2+b^2)}$	$\sqrt{(a^2+b^2)}$	$\frac{1}{2}\sqrt{(a^2+b^2)}$
<101>	$\sqrt{(a^2+c^2)}$	$\sqrt{(a^2+c^2)}$	$\sqrt{(a^2+c^2)}$	$\frac{1}{2}\sqrt{(a^2+c^2)}$
<011>	$\sqrt{(b^2+c^2)}$	$\sqrt{(b^2+c^2)}$	$\sqrt{(b^2+c^2)}$	$\frac{1}{2}\sqrt{(b^2+c^2)}$
<111>	$\sqrt{(a^2+b^2+c^2)}$	$\sqrt{(a^2+b^2+c^2)}$	$\frac{1}{2}\sqrt{(a^2+b^2+c^2)}$	$\sqrt{(a^2+b^2+c^2)}$

Like cubic and tetragonal, in orthorhombic system all <111> directions have the same unit translations $\sqrt{a^2+b^2+c^2}$. Therefore, the <111> family contains all eight members. They are: [111], $[\bar{1}11]$, $[1\bar{1}1]$, $[11\bar{1}]$, $[\bar{1}\,\bar{1}1]$, $[\bar{1}1\bar{1}]$, $[1\bar{1}\,\bar{1}]$ and $[\bar{1}\,\bar{1}\,\bar{1}]$.

Example 1.36 Draw $(\bar{1}11)$, $(1\bar{1}2)$ and $(\bar{2}10)$ planes in a cubic lattice.

Solution: Construct a cubic unit cell. Select the origin and the three crystallographic axes. Follow the said procedure and draw the given planes within the cubic unit cells as shown in Fig. 1.12.

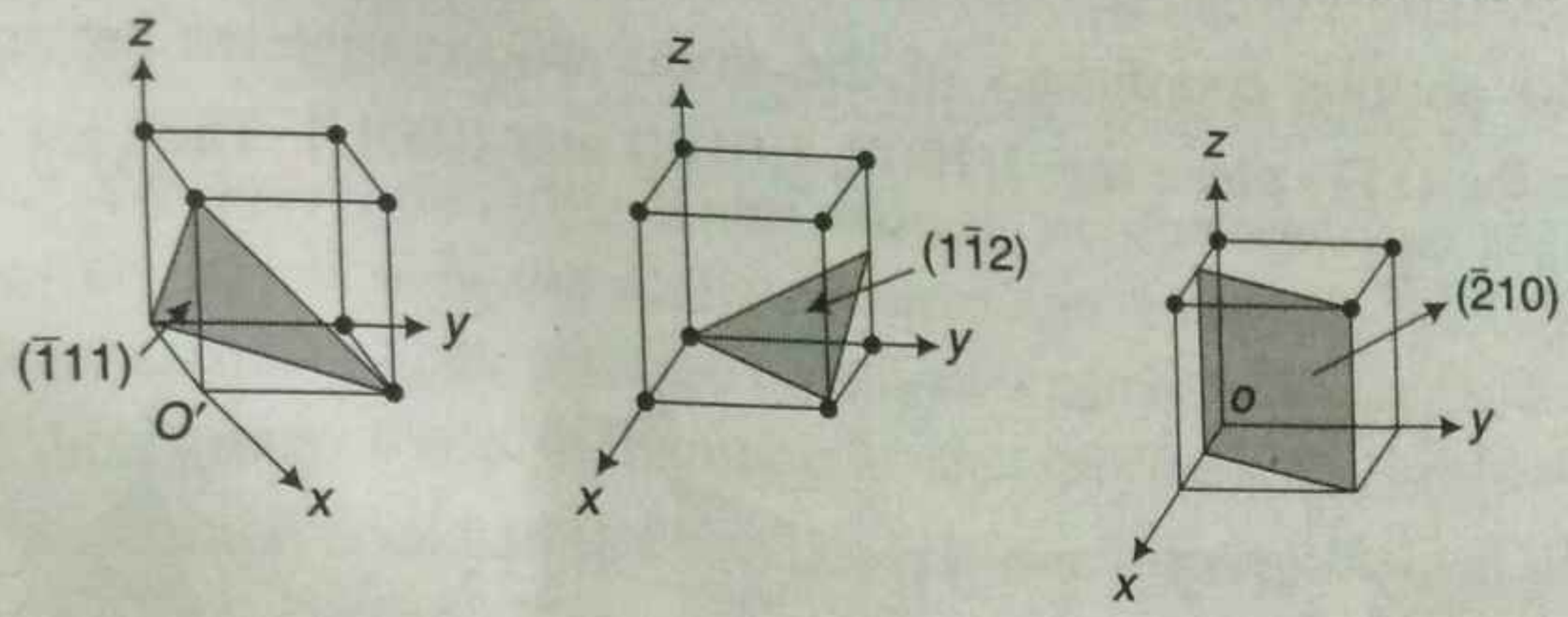


Fig. 1.12 (1̄11) (1$\bar{1}$2) and (2̄10) planes

Example 1.37 Determine the Miller indices of the line of intersection of the planes (1 $\bar{1}$ $\bar{1}$) and ($\bar{1}$ $\bar{1}$1). Also, show them diagrammatically.

Solution: Construct a cubic unit cell, select the origin and the three crystallographic axes. Now imagining the origin to be at O', draw (1 $\bar{1}$ $\bar{1}$) plane. Similarly, imagining the origin to be at O'', draw ($\bar{1}$ $\bar{1}$1) plane. Common direction of the two planes is shown as AB or BA (Fig. 1.13) whose Miller indices are: [101] or [$\bar{1}$0$\bar{1}$].

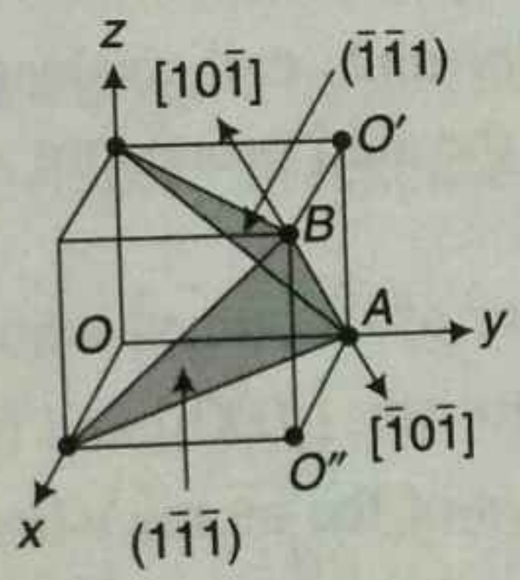


Fig. 1.13 (1 $\bar{1}$ $\bar{1}$) and ($\bar{1}$ $\bar{1}$1) planes

Example 1.38 Draw (100), (110) and (111) planes in *bcc* unit cells and list the position coordinates of the atoms whose centers are intersected by each of three planes.

Solution: Construct three bcc unit cells, select their origin and the three crystallographic axes. Follow the said procedure and draw the given planes within the unit cells as shown in Fig. 1.14.

(a) The position coordinates of the atoms whose centeres are intersected by the (100) plane are: [[100]], [[110]], [[101]] and [[111]. They are shown in Fig. 1.14a.

(b) The position coordinates of the atoms whose centeres are intersected by the (110) plane are: [[100]], [[010]], [[011]], [[101]] and $\left[\left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\right]\right]$. They are shown in Fig. 1.14b.

(c) The position coordinates of the atoms whose centeres are intersected by the (111) plane are: [[100]], [[010]] and [[001]]. They are shown in Fig. 1.14c.

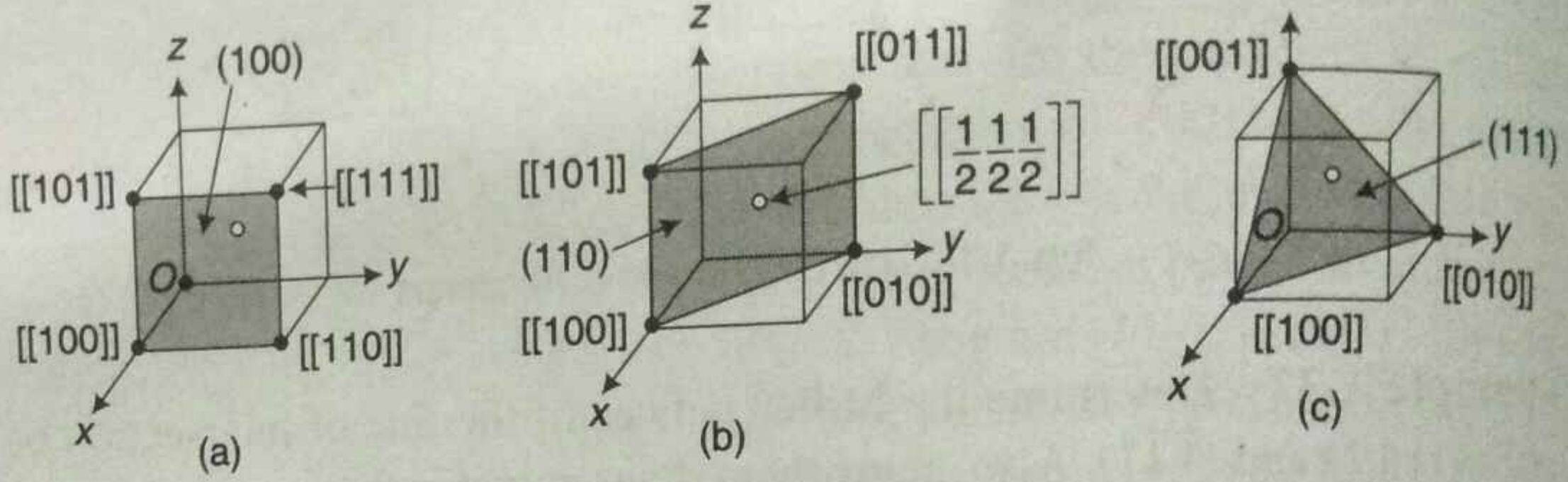


Fig. 1.14 Position coordinates intersected by (a) (100) plane, (b) (110) plane, (c) (111) plane

Example 1.39 Draw [100], [110] and [111] directions in an *fcc* unit cell and list the position coordinates of the atoms whose centeres are intersected by these direction vectors.

Solution: Construct an *fcc* unit cell, select the origin and the three crystallographic axes. Follow the said procedure and draw the given directions as shown in Fig. 1.15.

(a) The position coordinates of the atoms whose centeres are intersected by the [100] direction vector are: [[000]] and [[100]].

(b) The position coordinates of the atoms whore centeres are intersected by the [110] direction vector are: [[000]], $\left[\left[\frac{1}{2}\frac{1}{2}0\right]\right]$ and [[110]].

(c) The position coordinates of the atoms whose centeres are intersected by the [111] direction vector are: [[000]] and [[111]]. They are shown in Fig. 1.15.

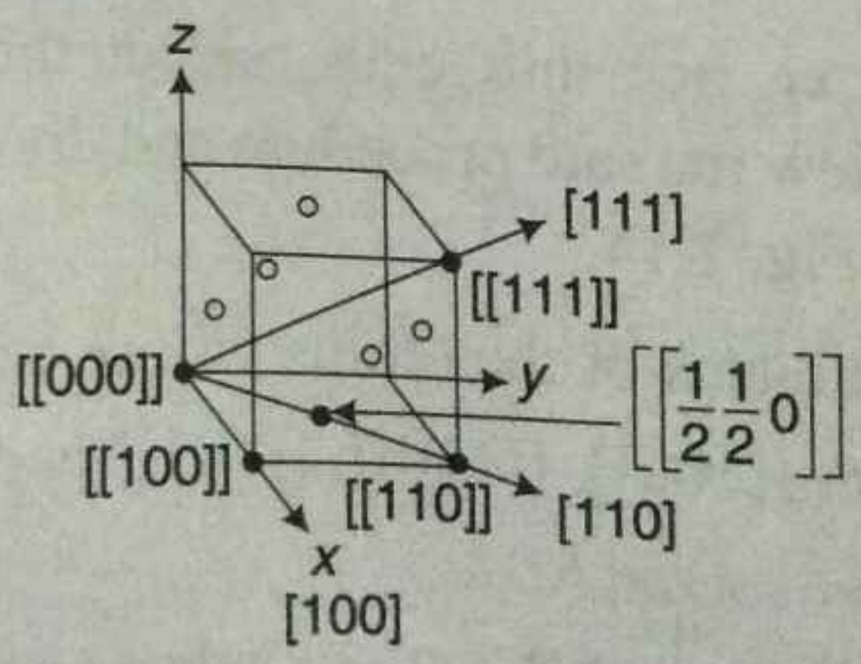


Fig. 1.15 [100], [110] and [111] directions in an *fcc* unit cell

Example 1.40 Draw [112], [121] and [220] directions in cubic unit cells.

Solution: We know that the Miller indices of direction and the position coordinates are identical if the digits are zero and 1 only. If the digits of the indices are greater than 1, the position coordinates can be obtained by dividing the indices of direction by the largest number so that they lie within the unit cube.

(a) The position coordinates for the [112] direction are obtained by dividing the indices of direction by 2. Thus the position coordinates become $\left[\left[\frac{1}{2}\ \frac{1}{2}\ 1\right]\right]$. The location of the position coordinates can be found by moving half distance each along x and y directions and a unit distance along z direction. The corresponding direction is shown in Fig. 1.16.

(b) Similar to the above, the position coordinates for the [121] direction are found to be $\left[\left[\frac{1}{2}\ 1\ \frac{1}{2}\right]\right]$ when they are divided by 2. The position coordinates and the corresponding crystallographic direction are shown in Fig. 1.16.

(c) Similarly, the position coordinates for the [220] direction are found to be [[110]] when they are divided by 2. The position coordinates and the corresponding crystallographic direction are shown in Fig. 1.16.

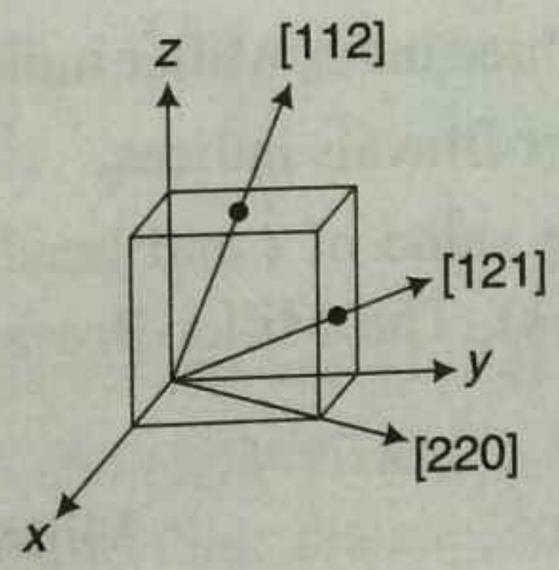


Fig. 1.16 [112], [121] and [220] directions

Example 1.41 Draw a $(1\bar{1}0)$ plane in a cubic unit cell. Find the Miller indices of directions that lie on this plane and show them.

Solution: Construct a cubic unit cell. Select the origin and the three crystallographic axes. Follow the said procedure and draw the given plane by shifting the origin from O to O' as shown in Fig. 1.17. The Miller indices of directions are also shown. They are: $[11\bar{1}]$, [111] and their opposite $[\bar{1}\,\bar{1}1]$ and $[\bar{1}\,\bar{1}\,\bar{1}]$.

Example 1.42 Determine the Miller indices of the line of intersection of planes (110) and (111). Also show them.

Solution: Consider the conventional orthogonal axes and construct a unit cell with O as the origin. Follow the said procedure and draw the given planes as

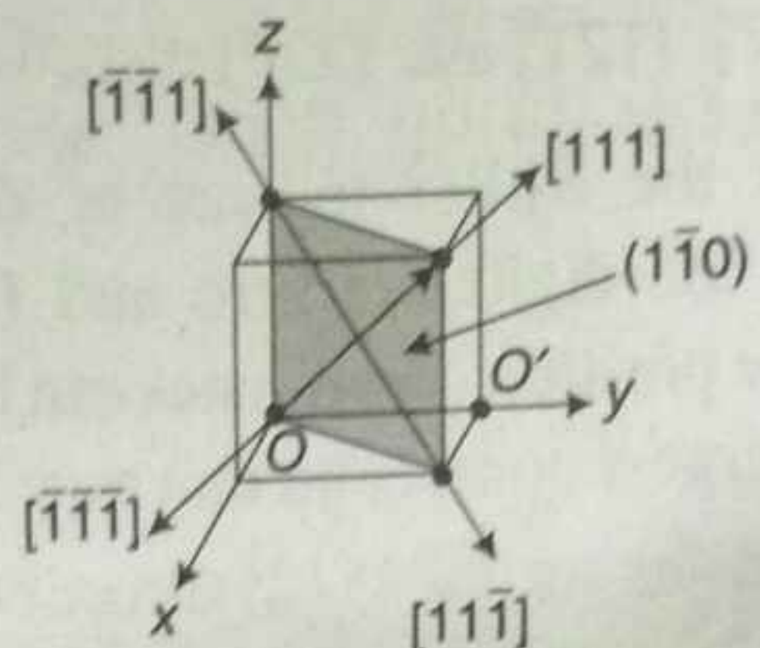


Fig. 1.17 (1$\bar{1}$0) plane and the directions that lie on this plane

shown in Fig. 1.18. Common direction to three planes is shown as *AB* or *BA* whose Miller indices: [1$\bar{1}$0] or [$\bar{1}$10].

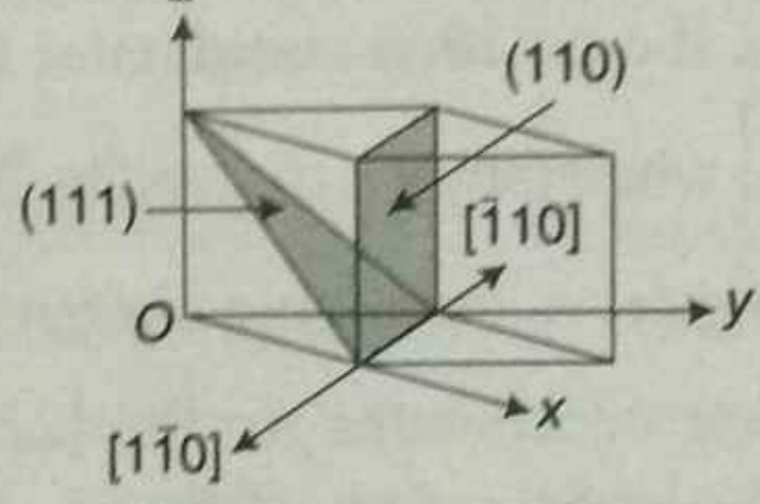


Fig. 1.18 (110) and (111) planes and their intersection

Example 1.43 Change the three index Miller indices (210), ($\bar{1}$13), (011), (246) and (4$\bar{2}$3) into four index Miller Bravais indices.

Solution: We determine the value of i and hence the Miller-Bravais indices using the formula $i = -(h + k)$. The Miller-Bravais indices are shown in the right column.

Miller indices	Miller Bravais indices
(210)	(21$\bar{3}$0) or (21.0)
($\bar{1}$13)	($\bar{1}$103) or ($\bar{1}$1.3)
(011)	(01$\bar{1}$1) or (01.1)
(246)	(24$\bar{6}$6) or (24.6)
(423)	(4$\bar{2}\bar{2}$3) or (4$\bar{2}$.3)

Example 1.44 Determine the Miller-Bravais indices for the directions [100], [110] and [111].

Solution:

Case I Given: [HKL] ≡ [100]

Now, the corresponding Miller Bravais indices can be obtained by using the following conversion formula:

$$h = \frac{(2H - K)}{3}, k = \frac{(2K - H)}{3}, i = -(h + k) \quad \text{and} \quad l = L.$$

Miller-Bravais indices	h	k	i	l
	$\frac{2}{3}$	$-\frac{1}{3}$	$-\frac{1}{3}$	0
Removing fraction	2	−1	−1	0

⇒ The required Miller-Bravais indices are: $[2\bar{1}\bar{1}0]$.

Case II Given: [HKL] ≡ [110]. The corresponding Miller-Bravais indices are:

Miller-Bravais indices	h	k	i	l
	$\frac{1}{3}$	$\frac{1}{3}$	$-\frac{2}{3}$	0
Removing fraction	1	1	−2	0

⇒ The required Miller-Bravais indices are: $[11\bar{2}0]$.

Case III Given: [HKL] ≡ [111]. The corresponding Miller-Bravais indices are:

Miller-Bravais indices	h	k	i	l
	$\frac{1}{3}$	$\frac{1}{3}$	$-\frac{2}{3}$	1
Removing fraction	1	1	−2	3

⇒ The required Miller-Bravais indices are: $[11\bar{2}3]$.

Example 1.45 Draw (111) and (222) planes in a simple cubic unit cell whose lattice parameter is a. Determine their distances from a parallel plane passing through the origin

Solution: We first determine the intercepts of both the planes which are: 1, 1, 1 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Mark these points inside the unit cell and draw the planes as shown in Fig. 1.19.

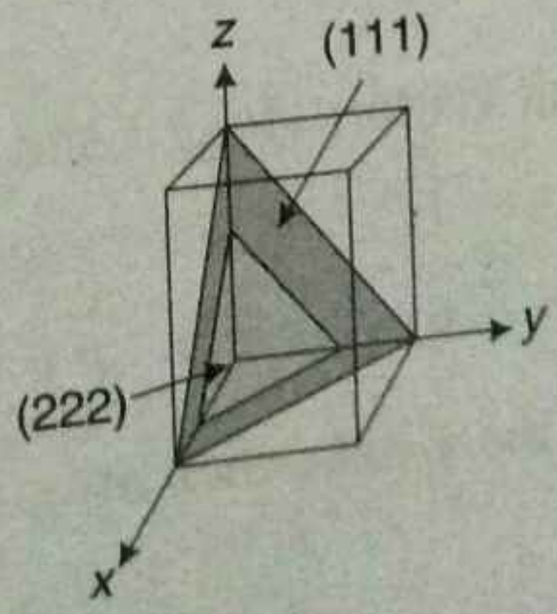


Fig. 1.19 Construction of (111) and (222) planes

Now, the distances of these planes w.r.t a parallel plane passing through the origin are determined by using the formula:

$$d = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$

Therefore, for (111) plane

$$d_{111} = \frac{1}{(1+1+1)^{1/2}} = \frac{1}{\sqrt{3}}$$

Similarly

$$d_{222} = \frac{1}{(4+4+4)^{1/2}} = \frac{a}{2\sqrt{3}}$$

Example 1.46 The distance between (111) planes in a face centered crystal is 2Å. Determine the lattice parameter and the atomic diameter.

Solution: Given: Miller planes (111), crystal is *fcc*,

$$d_{111} = 2\text{Å}, a = ?, D = ?$$

The interplanar distance between the (111) planes of an *fcc* crystal is given by

$$d_{111} = \frac{a}{\sqrt{3}}$$

or

$$2 = \frac{a}{\sqrt{3}}$$

$\Rightarrow$

$$a = 2\sqrt{3}\ \text{Å}.$$

Now, for an *fcc* crystal, the relationship between the lattice parameter and the diameter (or radius) of the atoms is given by

$$\sqrt{2}a = 4R = 2D$$

or

$$D = \frac{\sqrt{2}a}{2} = \frac{\sqrt{2} \times 2\sqrt{3}}{2} = \sqrt{6}\ \text{Å}.$$

Example 1.47 Prove that an oblique lattice gives rise to a centered rectangular lattice after reflection.

Proof: Let $\hat{i}$ and $\hat{j}$ be the unit vectors along x and y axis, respectively. Then for oblique lattice, we can write,

$$\vec{a} = a_x\hat{i} \quad \text{and} \quad \vec{b} = b_x\hat{i} + b_y\hat{j} \tag{1}$$

If we place a mirror along the x-axis, then after reflection let the new lattice vectors are a' and b' such that

$$\vec{a}' = a_x\hat{i} \quad \text{and} \quad \vec{b}' = b_x\hat{i} - b_y\hat{j} \tag{2}$$

If the lattice is invariant under the reflection, then a', b' must satisfy the condition $n_1\vec{a} + n_2\vec{b}$, where n_1 and n_2 are integers. This gives us

$$\vec{a}' = \vec{a} \quad \text{and} \quad \vec{b}' = n_1\vec{a} + n_2\vec{b}$$

$$= n_1 a_x \hat{i} + n_2(b_x\hat{i} + b_y\hat{j}) \text{ from eq. 1}$$

Equating this with $\vec{b}'$ in eq. 2, we have

$$b_x\hat{i} - b_y\hat{j} = (n_1 a_x + n_2 b_x)\hat{i} + n_2 b_y\hat{j}$$

Now comparing the coefficients of $\hat{i}$ and $\hat{j}$ on both sides, we have

$$b_x = n_1 a_x + n_2 b_x \quad \text{and} \quad -b_y = n_2 b_y \quad \text{or} \quad n_2 = -1$$

Therefore, $b_x = n_1 a_x - b_x$

$$\Rightarrow \qquad b_x = \frac{n_1 a_x}{2} \tag{3}$$

The simplest possible choice is $n_1 = 1$, so that $b_x = \frac{a_x}{2}$. Substituting these in eq. 1, we obtain

$$\vec{a} = a_x\hat{i} \quad \text{and} \quad \vec{b} = \frac{1}{2}a_x\hat{i} + b_y\hat{j} \tag{4}$$

The above choice ($n_1 = 1$) gives a centered rectangular lattice with $a \neq b$, $\phi = 90$.

Example 1.48 Show that $\tilde{1}$ (one "tilde") is equivalent to a mirror plane.

Solution: It is a combined operation of rotation and reflection. In this case, the proper 1-fold rotation will rotate the motif representing all space (here it is taken as *J*) through an angle of 0° or 360°, i.e. leaving it unchanged. Combining this with reflecting plane perpendicular to the rotation axis to produce a configuration as shown in Fig. 1.20. Which is identical to the configuration already encountered in Fig. 1.6c. Thus, the operation $\tilde{1}$ is equivalent to a reflection through a plane (specifically a mirror plane).

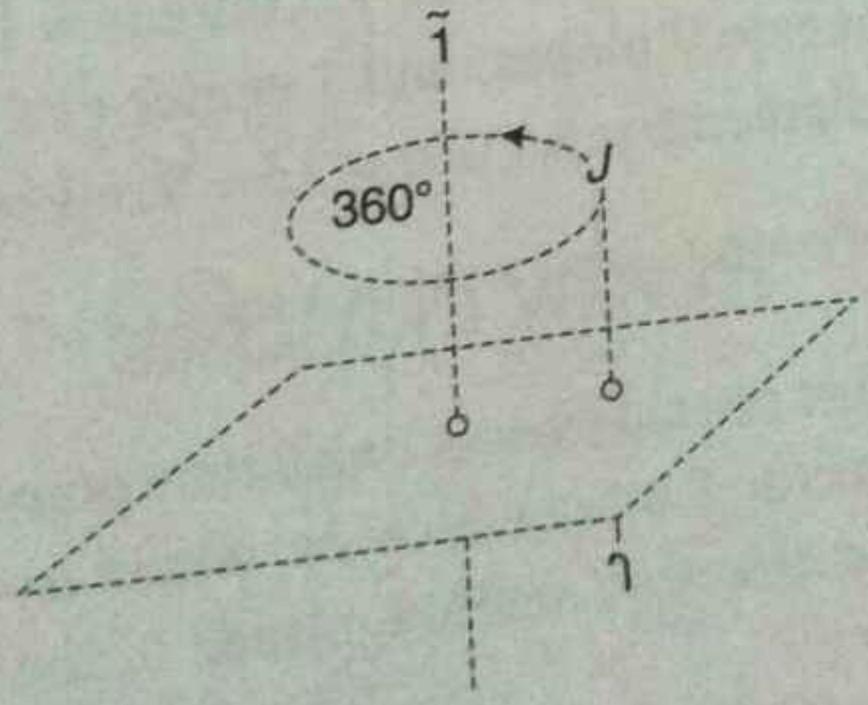


Fig. 1.20 Showing that $\tilde{1}$ ≡ mirror plane

Example 1.49 Show that $\tilde{2}$ is equivalent to an inversion center.

Solution: In this case, the proper 2-fold rotation will rotate the object (through an imaginary axis) through an angle 180° and then reflected across an imaginary plane placed at right angle to the imaginary rotation axis, the resulting configuration (Fig. 1.21) is identical to the configuration shown in Fig. 1.6d. Thus, the operation $\tilde{2}$ is equivalent to an inversion center.

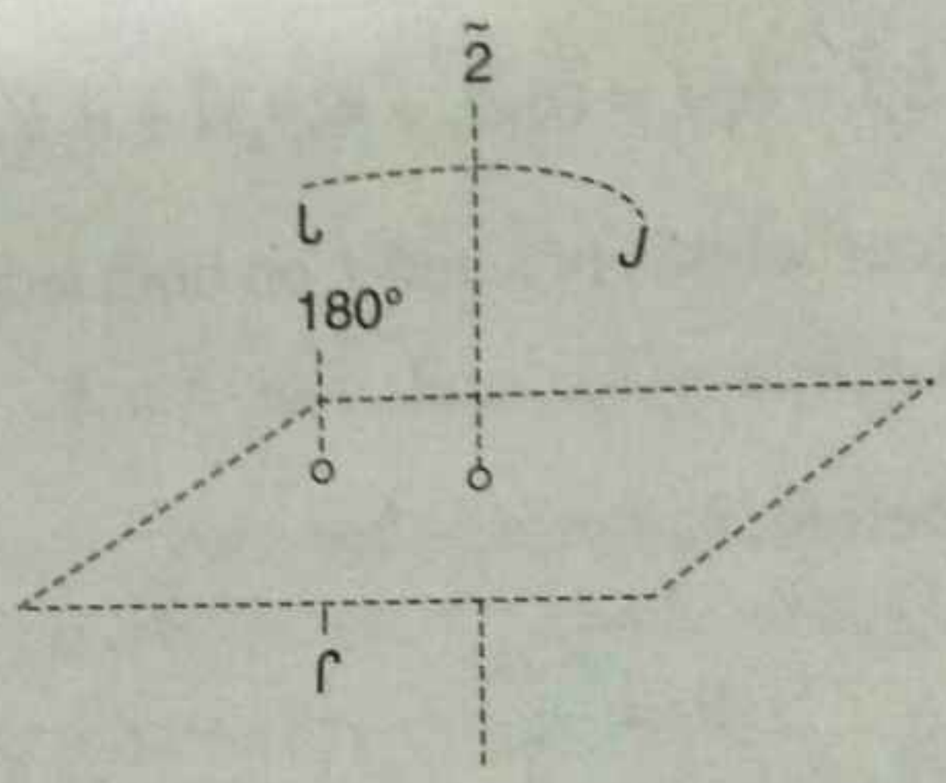


Fig. 1.21 Showing that $\tilde{2} \equiv$ inversion center

Example 1.50 Find the total number of symmetry elements that exist in a cube.

Solution: Looking at the Fig. 1.22, we find that there exist

(i) 2-fold axes parallel to the face diagonal and passing through the center of the cube. There are six such axes.

(ii) 3-fold rotoinversion axes passing through the body diagonal. There are four such axes.

(iii) 4-fold symmetry about an axis passing through the center of two opposite faces. There are three such symmetry axes.

(iv) Nine mirror planes bisecting the parallel faces, and connecting diagonal edges. All of them are passing through the center of the cube.

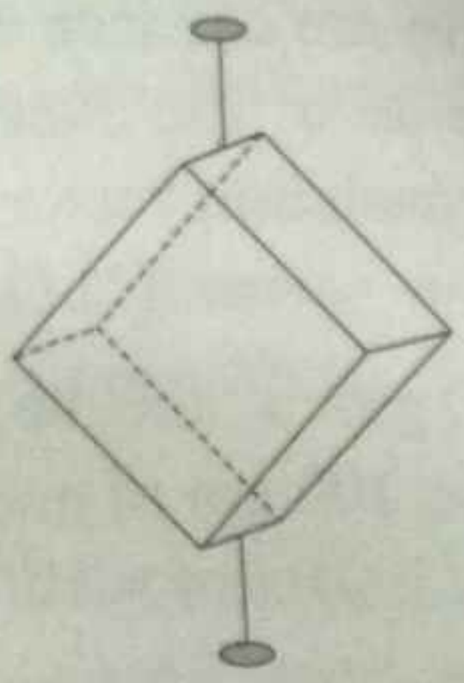
(v) One center of symmetry at the center of the cube.

Thus, there are: 6-diads + 4 triads + 3 tetrads = 13 axes, 3 surface planes + 6 diagonal planes = 9 planes, and 1 center of symmetry. Therefore, the total symmetry elements in a cube = 13 + 9 + 1 = 23.

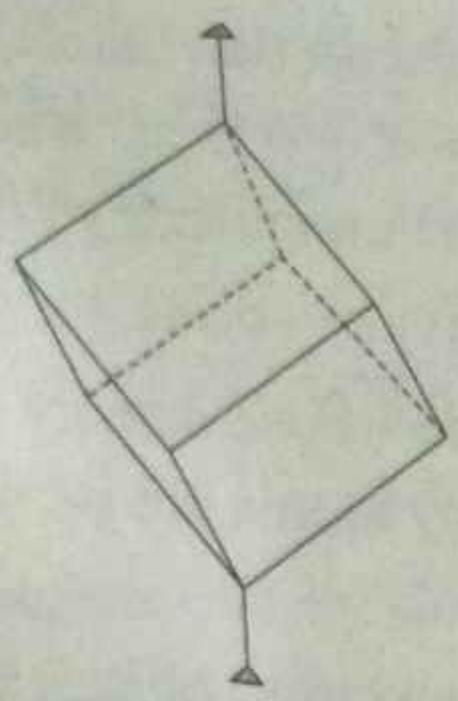
Review Problems

1.1 In an orthorhombic crystal system two lattice points are connected through the translation vector $T = 5a + 3b + 2c$, where $a = 1$ Å, $b = 2$ Å and $c = 3$ Å. Determine the direction and magnitude of the translation vector.

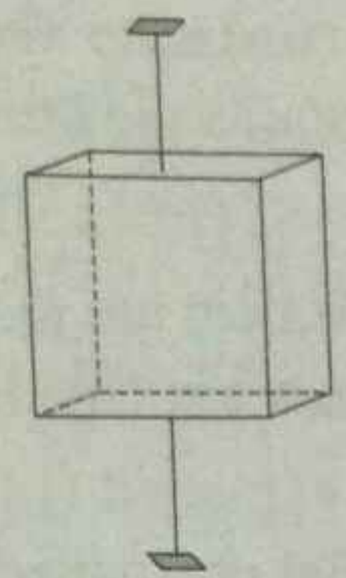
Ans. [532], 9.85 Å.



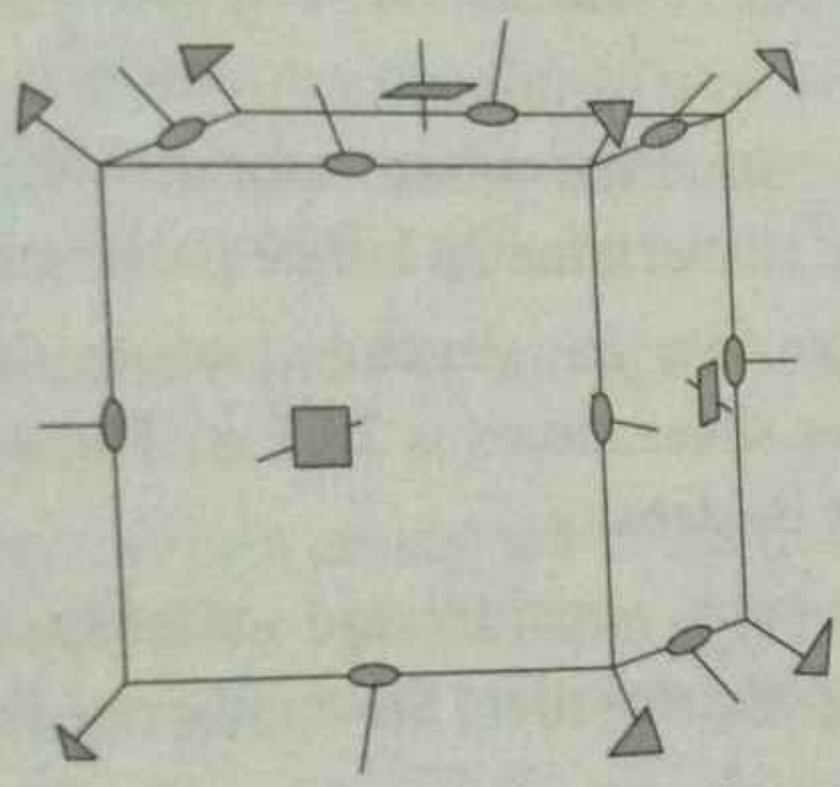
One of the diad-axes



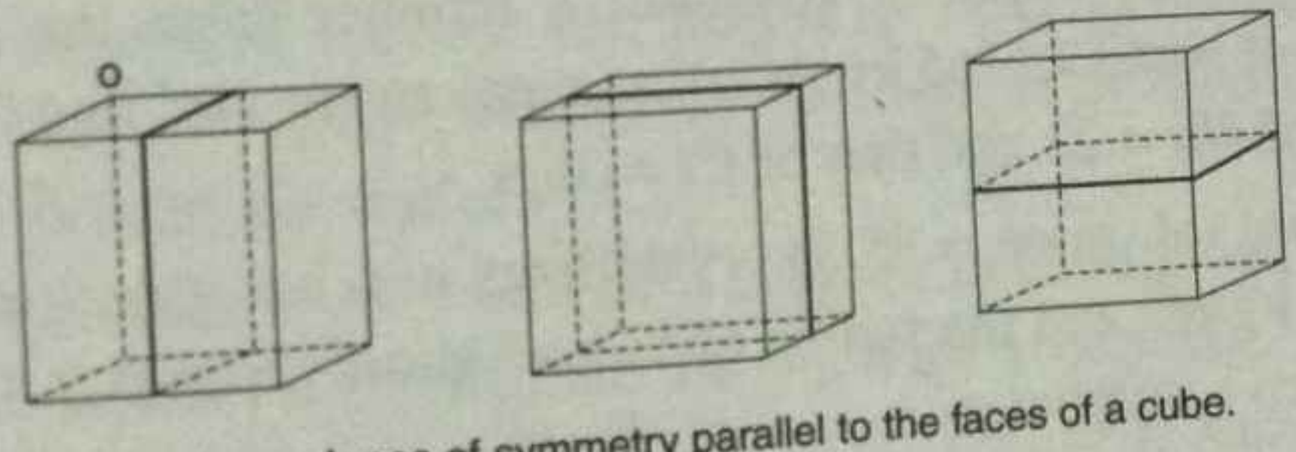
One of the triad axes and



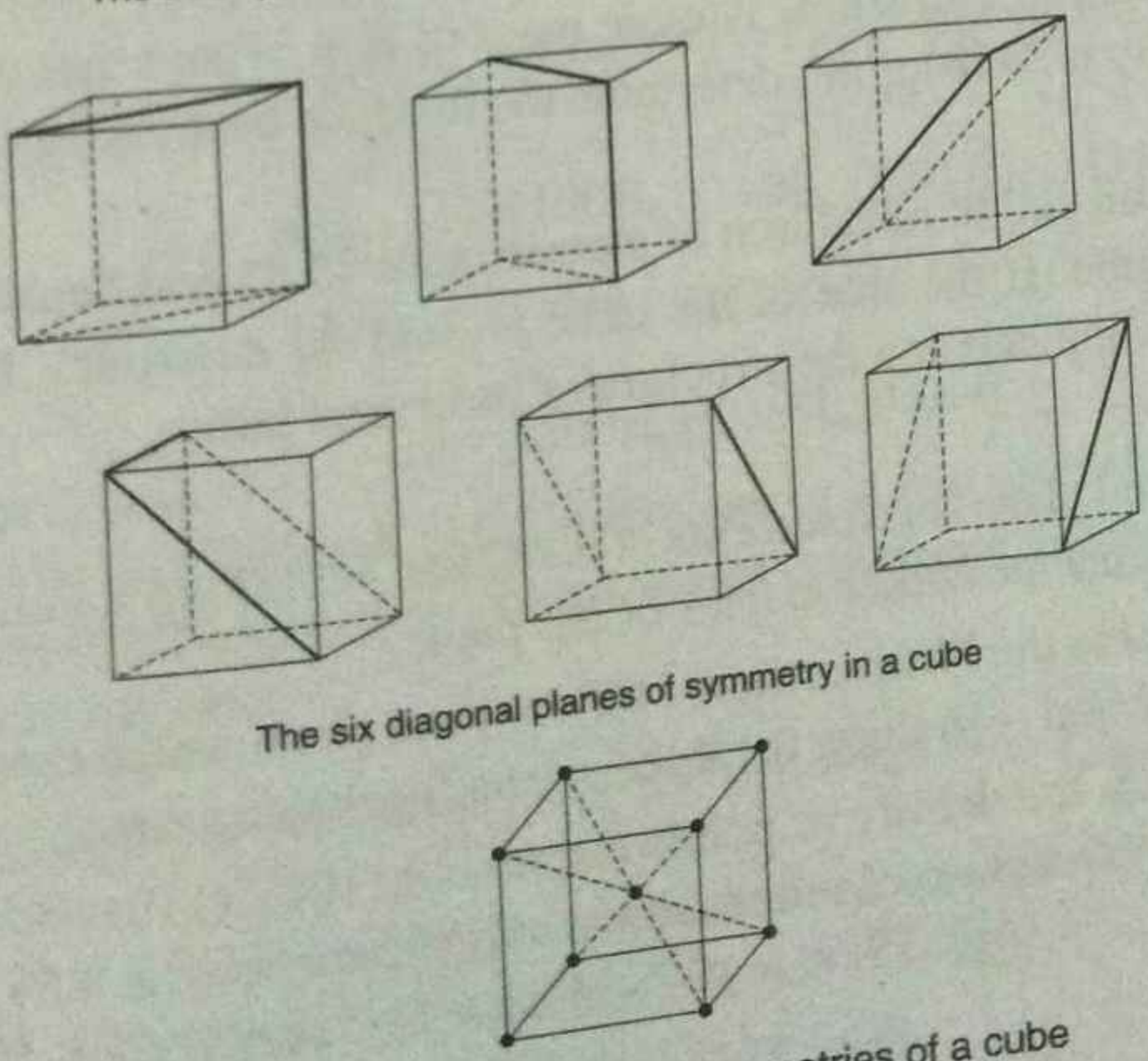
One of the tetrad axes of a cube



The thirteen axes of symmetry shown by a cube



The three planes of symmetry parallel to the faces of a cube.



The six diagonal planes of symmetry in a cube

Fig. 1.22 Showing various symmetries of a cube

1.2 In a simple cubic crystal system two lattice points are connected through the translation vector $T = a - b + c$, where side of the cube is 3 Å. Determine the direction and magnitude of the translation vector.

Ans. $[1\bar{1}1]$, $3\sqrt{3}$ Å.

1.3 An element has *fcc* structure whose density is 10 gm/m^3 and the unit cell parameter is 1 Å. How many atoms are present in 100 gm of material?

Ans. 4×10^{31} atoms

1.4 A metal crystallizes into two cubic phases *fcc* and *bcc*, whose unit cell parameters are 3.5 Å and 3.0 Å, respectively. Determine the ratio of their densities. *Ans.* 1.259

1.5 Sodium has *bcc* structure whose atomic weight is 23. Its density is 0.96×10^3 kg/m^3. Determine its lattice parameter. *Ans.* 4.3 Å

1.6 Silver crystallizes into *fcc* structure, where the distance between the nearest neighbour silver atoms is 2.87 Å. The atomic weight of silver is 107.88, calculate its density. *Ans.* 10.71×10^3 kg/m^3

1.7 Iron oxide has a cubic structure and its lattice parameter is 5 Å. If its density is 4000 kg/m^3, calculate the number of Fe^{2+} and O^{2-} ions present in each unit cell.

Ans. 4 Fe^{2+} and 4 O^{2-} ions

1.8 Determine the value of Avogadro's number from the following data: density of NaCl = 2165 kg/m^3, distance between Na^+ and Cl ions = 2.81 Å, At.wt. of Na = 23 and that of Cl = 35.5. *Ans.* 6.089×10^{26}

1.9 Rubidium (at. mass = 85.5) crystallizes into bcc structure. If its density is 1510 kg/m^3 and the radius of the rubidium atom is 2.48 Å, determine Avogadro's number.

Ans. 6.019×10^{26}

1.10 *KF* has NaCl structure. Atomic mass of K = 39 and that of F = 19. If its density is 2480 kg/m^3, determine the distance between K^+ and F^- ions in *KF*.

Ans. 2.69 Å

1.11 The unit cell of metal iron of atomic mass 55.85 and density 7860 kg/m^3 is a cube. If the side of the cube is 2.88 Å, determine the number of atoms/unit cell and the structure of its crystal lattice.

Ans. 2, structure is *bcc*

1.12 A crystal plane cuts intercepts of a, $b/2$ and $3c/2$ along x, y and z directions. Determine the Miller indices of the plane. *Ans.* (362)

1.13 Determine the Miller indices of the crystal plane which cuts intercepts of $2a$, $-3b$ and $-3c$ along the three crystallographic axes. *Ans.* $(3\bar{2}\bar{2})$

1.14 Calculate the density of points (atoms) in (100), (110) and (111) planes of a simple cubic polonium whose lattice parameter is 3.34 Å.

Ans. 89.64×10^{18}, 65.38×10^{18} and 51.75×10^{18} atoms/m^2

1.15 Calculate the density of points (atoms) in (100), (110) and (111) planes of *bcc* barium whose lattice parameter is 5.02 Å.

Ans. 3.97×10^{18}, 5.61×10^{18} and 2.29×10^{18} atoms/m^2

1.16 Calculate the density of atoms in (100), (110) and (111) planes of *fcc* copper whose lattice parameter is 3.61 Å.

Ans. 1.53×10^{19}, 1.08×10^{19}, and 1.77×10^{19} atoms/m^2

1.17 Calculate the linear atomic density along [100], [110] and [111] directions in *bcc* barium whose lattice parameter is 5.02 Å.

Ans. 1.99×10^9, 1.41×10^9 and 2.30×10^9 atoms/m

1.18 Calculate the linear atomic density along [100], [110] and [111] directions in *fcc* aluminum whose lattice parameter is 4.05 Å.

Ans. 2.47×10^9, 3.49×10^9 and 1.42×10^9 atoms/m

1.19 In a simple cubic crystal find the ratio of the intercepts on the three axes by the plane (123).

Ans. 6:3:2

1.20 The lattice parameters of a crystal are in the ratio $a : b : c = 0.52 : 1.00 : 0.48$. If a plane with Miller indices (121) cuts an intercept of 2.6 Å along the x-axis, find the length of the intercepts along y-and z-axes.

Ans. $l_2 = 2.5$ Å and $l_3 = 2.4$ Å

1.21 The coordinates of a lattice site nearest to the origin is given by $x = a/2$, $y = 1b$ and $z = (3/2)c$. Determine the indices of direction of the line passing through the lattice site.

Ans. [123]

1.22 The coordinates of two sites of a cubic lattice are given by [[100]] and [[111]], respectively. Calculate the angle between them.

Ans. 54.73°

1.23 Draw (100), (110) and (111) planes in *fcc* unit cells and list the position coordinates of the atoms whose centers are intersected by each of these planes.

Ans. (a) [[100]], [[110]], [[101]], [[111]]

(b) [[100]], [[010]], [[011]], [[101]], $\left[\left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\right]\right]$

(c) [[100]], [[010]], [[001]]

1.24 Draw [100], [110] and [111] directions in a *bcc* unit cell and list the position coordinates of the atoms whose centers are intersected by there direction vectors.

Ans. (a) [[000]], [[100]], (b) [[000]], [[110]], (c) [[000]], $\left[\left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\right]\right]$, [[111]]

1.25 Draw $[1\bar{1}1]$, $[2\bar{1}2]$ and $[0\bar{1}2]$ directions in a cubic unit cell.

1.26 Draw a [111] plane in a cubic unit cell and find the Miller indices of the directions that lie on this plane and show them

Ans. [101], $[1\bar{1}0]$, [011] or their apposites

1.27. Determine the Miller indices of the line of intersection of the planes (100) and $(00\bar{1})$ in a cubic unit cell. *Ans.* [010] or its opposite

1.28. Change the Miller indices (120), (123), $(\bar{1}24)$, $(2\bar{2}5)$ and (235) into Miller Bravais indices. *Ans.* $(12\bar{3}0)$, $(12\bar{3}3)$, $(\bar{1}2\bar{1}4)$, $(2\bar{2}05)$ and $(23\bar{5}_5)$

1.29. Determine the value of i in the following Miller Bravais indices (10.2), (12.5), (01.3), $(2\bar{1}.3)$ and $(3\bar{4}.6)$ *Ans.* $\bar{1}, \bar{3}, \bar{1}, \bar{1}, 1$

1.30 In a tetragonal crystal $a = b = 2.5$ Å and $c = 1.8$ Å. Determine the interplanar spacing between (111) planes. *Ans.* 1.26 Å

MULULTIPLE CHOICE QUESTIONS

1.1 The coordination number of a simple cubic (*sc*) structure is:

(a) 4 (b) 6 (c) 8 (d) 12

1.2 The coordination number of a *bcc* structure is:

(a) 4 (b) 6 (c) 8 (d) 12

1.3 The coordination number of a *fcc* structure is:

(a) 4 (b) 6 (c) 8 (d) 12

1.4 The coordination number of a *hcp* structure is:

(a) 3 (b) 6 (c) 9 (d) 12

1.5 If a rectangular object has 6 faces and 8 corners, the number of edges are:

(a) 6 (b) 8 (c) 12 (d) 16

1.6 The number of two dimensional lattices are:

(a) 3 (b) 5 (c) 7 (d) 9

1.7 Total number of macroscopic symmetry elements in a cube is

(a) 13 (b) 31 (c) 23 (d) 32

1.8 The number of molecules per unit cell of NaCl structure is:

(a) 1 (b) 2 (c) 4 (d) 8

1.9 The radius of identical sphere arranged in simple cubic form of side a is:

(a) $\frac{a}{2}$ (b) $\frac{a}{2\sqrt{2}}$ (c) $\frac{\sqrt{3}a}{2}$ (d) $\frac{\sqrt{3}a}{4}$

1.10 The radius of identical spheres arranged in *bcc* form of side a is:

(a) $\frac{a}{2}$ (b) $\frac{a}{2\sqrt{2}}$ (c) $\frac{\sqrt{3}a}{2}$ (d) $\frac{\sqrt{3}a}{4}$

1.11 The radius of identical spheres arranged in *fcc* form of side a is:

(a) $\frac{a}{2}$ (b) $\frac{a}{2\sqrt{2}}$ (c) $\frac{\sqrt{3}a}{2}$ (d) $\frac{\sqrt{3}a}{4}$

1.12 The number of crystallographically equivalent planes in the {100} family of a cubic crystal system is:
(a) 4 (b) 6 (c) 8 (d) 12

1.13 The number of crystallographically equivalent planes in the {110} family of a cubic crystal system is:
(a) 4 (b) 6 (c) 8 (d) 12

1.14 The number of crystallographically equivalent planes in the {111} family of a cubic crystal system is:
(a) 4 (b) 6 (c) 8 (d) 12

1.15 The number of a crystallographically equivalent directions in the <100> family of a cubic crystal system is:
(a) 4 (b) 6 (c) 8 (d) 12

1.16 The number of cryptallographically equivalent directions in the <110> family of a cubic crystal system is:
(a) 4 (b) 6 (c) 8 (d) 12

1.17 The number of crystallographically equivalent directions in the <111> family of a cubic crystal system is:
(a) 4 (b) 6 (c) 8 (d) 12

1.18 The number of crystallographically equivalent directions in the <100> family of a tetragonal crystal system is:
(a) 4 (b) 6 (c) 8 (d) 12

1.19 The number of crystallographically equivalent directions in the <110> family of a tetragonal crystal system is;
(a) 4 (b) 6 (c) 8 (d) 12

1.20 The number of crystallographically equivalent directions in the <101> or <011> family of a tetragonal crystal system is:
(a) 4 (b) 6 (c) 8 (d) 12

1.21 The number of crystallographically equivalent directions in the <111> family of a tetragonal crystal system is:
(a) 4 (b) 6 (c) 8 (d) 12

1.22 The pure rotational symmetry which is not possible in crystalline solid is:
(a) 2-fold (b) 3-fold (c) 4-fold (d) 5-fold

1.23 The number of point groups in a two-dimensional crystal system is:
(a) 5 (b) 10 (c) 15 (d) 20

1.24 The number of point groups in a 3-dimensional crystal system is:
(a) 8 (b) 16 (c) 24 (d) 32

1.25 The angle between [001] and [111] directions in a cubic crystal is:

(a) 45° (b) 50° (c) 55° (d) 60°

1.26 The angle between [110] and [111] directions in a cubic crystal is:

(a) 30° (b) 35° (c) 40° (d) 45°

1.27. The angle between [001] and [101] directions in a cubic crystal is:

(a) 30° (b) 35° (c) 40° (d) 45°

1.28 The ratio of low index interplanar spacings $d_{100} : d_{110} : d_{111}$ in simple cubic (*sc*) is:

(a) $1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$ (b) $1 : \sqrt{2} : \sqrt{3}$ (c) $1 : \sqrt{2} : \frac{1}{\sqrt{3}}$ (d) $1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}$

1.29 The ratio of low index interplanar spacings $d_{100} : d_{110} : d_{111}$ in *bcc* is:

(a) $1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$ (b) $1 : \sqrt{2} : \sqrt{3}$ (c) $1 : \sqrt{2} : \frac{1}{\sqrt{3}}$ (d) $1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}$

1.30 The ratio of low index interplanar spacings $d_{100} : d_{110} : d_{111}$ in *fcc* is:

(a) $1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$ (b) $1 : \sqrt{2} : \sqrt{3}$ (c) $1 : \sqrt{2} : \frac{1}{\sqrt{3}}$ (d) $1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}$

Answers

1. (b)	2. (c)	3. (d)	4. (d)	5. (c)	6. (b)	7. (c)
8. (c)	9. (a)	10. (b)	11. (d)	12. (b)	13. (d)	14. (c)
15. (b)	16. (d)	17. (c)	18. (a)	19. (a)	20. (c)	21. (c)
22. (d)	23. (b)	24. (d)	25. (c)	26. (b)	27. (d)	28. (a)
29. (c)	30. (d)					

CHAPTER 2

Atomic Shape and Size

IMPORTANT FORMULAE

2.1 For a revolving electron, the force of attraction between electron and nucleus must be equal to the centrifugal force on the electrom i.e

$$\frac{(Ze)(e)}{4\pi \in_0 \gamma_n^2} = \frac{mv_n^2}{r_n}$$

where the suffix n appears for the n^{th} orbit (also is the principal quantum number).

2.2 The velocity of the electron in the n^{th} orbit given by Bohr's quantum condition is

$$v_n = \frac{Ze^2}{n2h \in_0}$$

2.3 According to Bohr's model of hydrogen atom, the radius of n^{th} orbit is given by

$$r_n = \frac{n^2 h^2 \in_0}{\pi m Ze^2}$$

For
$$n = 1, r_1 = \frac{h^2 \in_0}{\pi m Ze^2}$$

Therefore, $r_n = n^2 r_1$

2.4 Bohr's quantum condition for a stationary orbit is given as

$$mv_n r_n = n\frac{h}{2\pi}$$

$$\text{Therefore } n = \frac{2\pi m v_n r_n}{h}$$

This is the number of waves permitted in an orbit.

2.5 The orbital frequency of the electron is given by

$$f_n = \frac{\text{Velocity of electron}}{\text{Orbital circumference}} = \frac{v_n}{2\pi r_n}$$

Substituting the values of v_n and r_n from above, the orbital frequency of the election becomes:

$$f_n = \frac{Z^2 me^4}{4\epsilon_0^2 n^3 h^3}$$

2.6 Energy expressions of the election in the n^{th} orbit are given as

(i) $P.E$ of the election $= \dfrac{-Ze^2}{4\pi\epsilon_0 r_n}$

(ii) $K.E$ of the election $= \dfrac{Ze^2}{8\pi\epsilon_0 r_n} = -\dfrac{1}{2} P.E$

(iii) Total energy of the electron $E = K.E + P.E$

or $$E = \frac{-Ze^2}{8\pi\epsilon_0 r_n}$$

Substituting the value of r_n from above, we obtain

$$E_n = \frac{-mZ^2e^4}{8\epsilon_0 n^2 h^2} = -\frac{B}{n^2} = \frac{-13.6}{n^2} \text{ eV for hydrogen atom.}$$

2.7 If E_i and E_f are energies associated with the orbits of principal quantum numbers n_i and n_f respectively ($n_i < n_f$), the frequency of radiation emitted is given by

$$h\nu = E_i - E_f$$

If an electron jumps from an outer, (initial) orbit n_2 of higher energy to an inner (final) orbit n_1 of lower energy and substituting the values of E_i and E_f from above, we obtain,

$$h\nu = (E_i - E_f) = -\left[\frac{mz^2e^4}{8\epsilon_0^2 n_2^2 h^2}\right] + \left[\frac{mz^2e^4}{8\epsilon_0^2 n_1^2 h^2}\right]$$

$$= \frac{mz^2e^4}{8\epsilon_0^2 h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

2.8 It an ionic crystal, the radius of an ion is given by

$$r_{\text{ion}} = \frac{c_n}{Z - S} = \frac{c_n}{Z_{\text{eff}}}$$

where c_n is a constant to be determined by the quantum number, Z_{eff} is the effective nuclear charge, and S is a screening constant. C_n take

the same value for all numbers of an isostructural series (ions having identical electronic structure)

For an ion with : neon configuration, $S = 4.52$ per electron charge, argon configuration, $S = 11.25$ per electron charge.

2.9 According to Pauling, an empirical formula for determining the percentage of ionic character of the bond is given by

$$p = 16|X_A - X_B| + 3.5|X_A - X_B|^2$$

where $X_A - X_B$ are electronegativity values of A and B ions.

Solved Examples

Example 2.1 At what speed must the electron revolve round the nucleus of hydrogen atom in its ground state in order that it may not be pulled into the nucleus by electrostatic attraction. The radius of the first Bohr orbit is 0.53Å.

Solution: Given: $r = 0.53$ Å $= 0.53 \times 10^{-10}$ m, for H_2 atom $z = 1$, v = ?

We know that in hydrogen atom the Coulomb's force of attraction between the nucleus and the electron must be balanced by the Newtonian centrifugal force so that the electron continue to revolve with a velocity v in a circular orbit of say radius r. Mathematically, this can be written as

$$\frac{e^2}{4\pi\epsilon_0 r^2} = \frac{mv^2}{r}$$

or

$$v = e \times \sqrt{\frac{1/4\pi\epsilon_0}{mr}}$$

$$= 1.6 \times 10^{-19} \times \sqrt{\frac{9 \times 10^9}{9.1 \times 10^{-31} \times 0.53 \times 10^{-10}}}$$

$$= 1.6 \times 10^{-19} \times 1.366 \times 10^{25}$$

$$= 2.18 \times 10^6 \text{ m/s}$$

Example 2.2 The speed of electrons in the innermost orbit of the hydrogen atom is 2.18×10^6 m/s. Determine the radius of the orbit and the time taken by the electron in completing one revolution of this orbit.

Solution: Given: For innermost orbit, $n = 1$, for hydrogen atom $Z = 1$, $v_1 = 2.18 \times 10^6$ m/s, $r_1 = ?$.

From Bohr's quantum condition for a stationary orbit, we know that

$$mv_n r_n = \frac{nh}{2\pi}$$

For $n = 1$, $r_1 = \frac{h}{2\pi m v_1}$

$$= \frac{6.626 \times 10^{-34}}{2 \times 3.14 \times 9.1 \times 10^{-31} \times 2.18 \times 10^{6}}$$

$$= 0.53 \times 10^{-10}\,\text{m} = 0.53\ \text{Å}$$

Time taken by the electron in completion one revolution of the first orbit is

$$t = \frac{\text{Distance travelled}}{\text{Velocity}}$$

$$= \frac{2\pi r_1}{v_1}$$

$$= \frac{2 \times 3.14 \times 0.53 \times 10^{-10}}{2.18 \times 10^{6}}$$

$$= 1.53 \times 10^{-16}\,\text{S}$$

Example 2.3 Find out the radius of the Bohr's fifth orbit for hydrogen atom. Also determine the velocity of electron and the number of waves in that orbit. The radius of the first Bohr orbit is 0.53 Å.

Solution: Given: $n = 5$, $r_1 = 0.53\ \text{Å} = 0.53 \times 10^{-10}$ m, $r_5 = ?$, number of waves = ?

We know that the radius of the n^{th} orbit is given by

$$r_n = \frac{n^2 h^2 \in_0}{\pi m z e^2}$$

Further, for $Z = 1$ (hydrogen atom) and $n = 5$,
the radius of the fifth orbit is

$$r_5 = \frac{25 \times (6.626 \times 10^{-34})^2 \times 8.854 \times 10^{-12}}{3.14 \times 9.1 \times 10^{-31} \times (1.6 \times 10^{-19})^2}$$

$$= 13.28 \times 10^{-10}$$

$$= 13.28\text{Å}$$

Now, the velocity in the n^{th} orbit is given by

$$v_n = \frac{Ze^2}{n2h\in_0}$$

For $n = 5$ and $Z = 1$, the velocity of the electron is the fifth orbit

$$v_5 = \frac{e^2}{10h\in_0}$$

$$= \frac{(1.6 \times 10^{-19})^2}{10 \times (6.626 \times 10^{-34} \times 8.854 \times 10^{-12})}$$

$$= 4.36 \times 10^{5}\ \text{m/s}$$

According to the Bohr's quantum condition, the number of waves in the n^{th} stationary orbit is (say)

$$n' = \frac{2\pi m v_n r_n}{h}$$

For $n = 5$ (the fifth orbit)

$$n' = \frac{2\pi m v_5 r_5}{h}$$

$$= \frac{2 \times 3.14 \times 9.1 \times 10^{-31} \times 4.36 \times 10^{5} \times 13.28 \times 10^{-10}}{6.626 \times 10^{-34}}$$

$$= \simeq 4.99 = 5$$

$\Rightarrow$ Number of waves is the same as that of the order of the orbit.

Example 2.4 Electron energies 10.2 eV and 12.09 eV can cause radiation to be emitted from hydrogen atom. Calculate in each case, the principal quantum number of the orbit to which an electron in the hydrogen atom is raised and the wave length of radiation if it drops back to the ground state.

Solution: Given: $E_n = 10.2$ eV, $E_{n'} = 12.09$ eV, $n = ?$, $n' = ?$

$$\lambda = ?, \lambda' = ?$$

We know that the total energy in the n^{th} orbit is given by

$$E_n = -\left(\frac{mz^2e^4}{8E_0^2n^2h^2}\right) \quad (1)$$

Substituting the values of constants, we obtain,

$$E_n = -\frac{13.6}{n^2}\text{ eV} \quad (2)$$

where n is the principal quantum number. For $n = 1$, we have $E_1 = -13.6$ eV. This corresponds to the ground state energy of the atom, and is called the first ionization potential of hydrogen atom. Similarly, for $n = 2$, we have $E_2 = -\frac{13.6}{4} = -3.4$ eV (second ionization potential) and for $n = 3$, we have

$$E_3 = -\frac{13.6}{9} = -1.51 \text{ (third ionization potential)}$$

Now, we can obtain the energies between the orbits,

$$n_2 - n_1 = -3.4 - (-13.6) = 10.2 \text{ eV}$$

Similarly,

$$n_3 - n_1 = -1.51 - (-13.6) = 12.09 \text{ eV}$$

These energies correspond to the excited states having principal quantum numbers as 2 and 3, respectively.

Further, an atom can absorb or radiate energy if the electron jumps from an inner orbit or falls from an outer orbit to an inner orbit. If E_i and E_f are energies associated with the orbits of principal quantum number n_i and n_f ($n_i < n_f$) respectively, the wavelength of the radiation emitted is given by

$$\frac{hc}{\lambda} = E_i - E_f = \frac{mZ^2e^4}{8E_0h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= 13.6\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ in eV}$$

$$= 13.6 \times 1.6 \times 10^{-19}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ in Joules}$$

Thus, for $n_1 = 1$ and $n_2 = 2$ or $n = 2$ to 1(or $L \rightarrow K$) transition, we have

$$\frac{hc}{\lambda} = 13.6 \times 1.6 \times 10^{-19}\left(\frac{1}{1} - \frac{1}{4}\right)$$

$$= 13.6 \times 1.6 \times 10^{-19} \times \frac{3}{4}$$

or

$$\lambda \doteq \frac{4hc}{13.6 \times 1.6 \times 10^{-19} \times 3}$$

$$= \frac{4 \times 6.626 \times 10^{-34} \times 3 \times 10^8}{13.6 \times 1.6 \times 10^{-19} \times 3}$$

$$= 1218 \text{ Å}$$

Similarly, for $n = 3$ to 1 (or $M \rightarrow K$) transition, we have

$$\lambda = \frac{9 \times 6.626 \times 10^{-34} \times 3 \times 10^8}{13.6 \times 1.6 \times 10^{-19} \times 8}$$

$$= 1027 \text{ Å}$$

Example 2.5 Find out the number of waves made by a Bohr electron in one complete revolution in its third orbit.

Solution: In general, the number of waves made by a Bohr electron in an orbit is equal to its quantum number. Thus, according to Bohr's postulate of angular momentum, in the third orbit is

$$mvr = 3\left(\frac{h}{2\pi}\right) \qquad (1)$$

However, according to de Broglie relationship, the wave length is

$$\lambda = \frac{h}{mv} \qquad (2)$$

Substituting for mv from (2) into (1), we have

$$\left(\frac{h}{\lambda}\right)r = 3\left(\frac{h}{2\pi}\right)$$

or $$3\lambda = 2\pi r$$

This tells us that the circumference of the third orbit is equal to 3 times the wave length associated with the electron i.e the electron makes 3 waves in one revolution of the third orbit as shown in Fig. 2.1

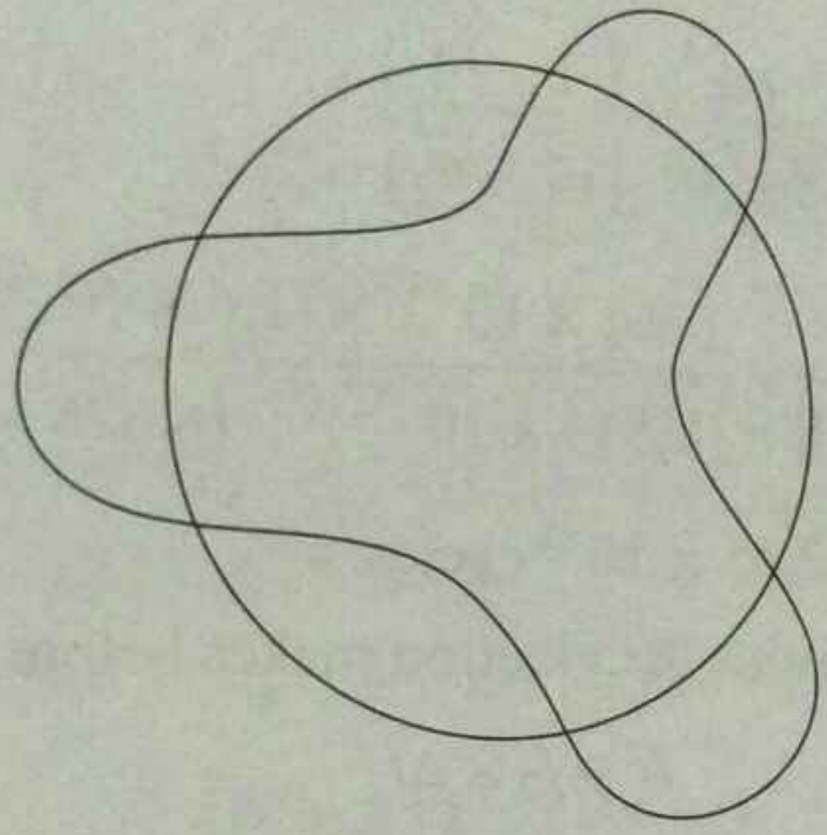


Fig. 2.1 The number of wavelengths in the third occur

Example 2.6 In a hydrogen atom, determine (a) the frequencies of revolution (orbital frequencies) of electrons in $n = 1$ and $n = 2$ Bohr orbit. (b) the frequency of the photon emitted when an electron in an orbit $n = 2$ drops to an orbit $n = 1$ and (c) how many revolutions does an electron in the $n = 2$ orbit make before it drops to an orbit $n = 1$ (the average life time of an excited state is about 10^{-8} s)?

Solution: Given: Bohr orbits $n = 1$, $n = 2$, for hydrogen atom, $Z = 1$, average life time of an exited state $\simeq 10^{-8}$ s, (a) $f_1 = ?, f_2 = ?$ (b) $v = ?$ (c) the revolution in the orbit $(n = 2) = ?$

(a) The orbital frequency of the n^{th} Bohr orbit is

$$f_n = \frac{mc^4}{4\epsilon_0^2 n^3 h^3}$$

For $n = 1$, we have

$$f_1 = \frac{me^4}{4\epsilon_0^2 h^3}$$

$$= \frac{9.1 \times 10^{-31} \times (1.6 \times 10^{-19})^4}{4 \times (8.854 \times 10^{-12})^2 \times (6.626 \times 10^{-34})^3}$$

$$= 6.54 \times 10^{15} \text{ revolutions/s}$$

Similarly, for $n = 2$, we have

$$f_2 = \frac{1}{2^3}(f_1)$$

$$= \frac{f_1}{8} = \frac{6.54 \times 10^{15}}{8}$$

$$= 8.17 \times 10^{14} \text{ revolutions/s}$$

(b) Frequency of the photon emitted during the $n_1 \rightarrow n_2$ transition is given by

$$\nu = \frac{me^4}{8\epsilon_0^2 h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$= \frac{9.1 \times 10^{-31} \times (1.6 \times 10^{-19})^4}{8 \times (8.854 \times 10^{-12})^2 \times (6.626 \times 10^{-34})^3} \times \frac{3}{4}$$

$$= 2.45 \times 10^{15} \text{ cycles/s}$$

(c) The number of revolutions the electron makes before it drops is

$$N = f_2 \times \Delta t$$

$$= 8.17 \times 10^{14} \times 10^{-8}$$

$$= 8.17 \times 10^6 \text{ revolutions}$$

Example 2.7 An electron in a hydrogen atom in its ground state absorbs 1.5 times the minimum energy required for it to escape from the atom. Determine the velocity of the electron and the wavelength associated with it.

Solution: Given: Energy absorbed by (electron) hydrogen atom = 1.5 E_1, where E_1 = 13.6 eV (the energy of the electron in the first orbit, i.e the ground state of the hydrogen atom), $m = 9.1 \times 10^{-31}$ kg, v = ?, λ = ?

We know that the amount of energy required to remove the electron from the first orbit of the hydrogen atom = 13.6 eV

The amount of the additional energy = $1.5 \times 13.6 - 13.6$

$$= 6.8 \text{ eV}$$

$$= 6.8 \times 1.6 \times 10^{-19} \text{ J}$$

The additional energy is converted into *K.E*, given by

$$K.E = \frac{1}{2} m\text{v}^2$$

or

$$\text{v} = \left(\frac{2 \times K.E}{m}\right)^{1/2}$$

$$= \left(\frac{2 \times 6.8 \times 1.6 \times 10^{-19}}{9.1 \times 10^{-31}}\right)^{1/2}$$

$$= 1.55 \times 10^6 \text{ m/s}$$

Further,

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 1.55 \times 10^{6}}$$

$$= 4.7 \times 10^{-10}\ \text{m}$$

$$= 4.7\ \text{Å}$$

Example 2.8 In a hydrogen atom, an electron jumps from the second orbit to the first orbit. Calculate the frequency of radiation emitted and the wavelength of the radiation.

Solution: Given: Electron jumps from $n = 2$ to $n = 1$ orbit, $\nu = ?$, $\lambda = ?$

We know that the energy of an electron in the n^{th} orbit is given by

$$E_n = -\frac{13.6}{n^2}\ \text{eV}$$

For $n = 1$, $E_1 = -13.6\ \text{eV}$

and $n = 2$, $E_2 = -\frac{13.6}{4} = -3.4\ \text{eV}$

The amount of energy released by the electron in jumping from $n = 2$ to $n = 1$ orbit is

$$\Delta E = E_2 - E_1 = -3.4 + 13.6$$

$$= 10.2\ \text{eV}$$

$$= 10.2 \times 1.6 \times 10^{-19}\ \text{J}$$

$$= 16.32 \times 10^{-19}\ \text{J}$$

Since, $\Delta E = h\nu$

or $\nu = \frac{\Delta E}{h} = \frac{16.32 \times 10^{-19}}{6.626 \times 10^{-34}}$

$$= 2.46 \times 10^{15}\ \text{cycles/s}$$

Further,

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^{8}}{2.46 \times 10^{15}}$$

$$= 1.22 \times 10^{-7}\ \text{m}$$

$$= 1220\ \text{Å}$$

Example 2.9 Electromagnetic radiation of wavelength 2420 Å is just sufficient to ionize the sodium atom. Calculate its ionization energy.

Solution: Given: $\lambda_{ion}(Na) = 2420\ \text{Å} = 2420 \times 10^{-10}$ m, $E_{ion}(Na) = ?$

We know that,

$$\nu_{ion} = \frac{c}{\lambda_{ion}} = \frac{3 \times 10^8}{2420 \times 10^{-10}}$$

$$= 1.24 \times 10^{15} \text{ cycle/s}$$

Further,

$$E_{ion} = h\nu_{ion}$$

$$= 6.626 \times 10^{-34} \times 1.24 \times 10^{15}$$

$$= 8.216 \times 10^{-19} \text{ J}$$

$$= \frac{8.216 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= 5.14 \text{ eV}$$

Example 2.10 The electron energy of hydrogen atom in the n^{th} Bohr's orbit is given by

$$E_n = -\frac{21.79 \times 10^{-19}}{n^2} \text{ J}.$$

Calculate the energy required to remove an electron completely from the orbit $n = 2$. Determine the wavelength of the light that can be used to cause this transition.

Solution: Given: $E_n = -\frac{21.79 \times 10^{-19}}{n^2}$ J, $n_i = 2$, $n_f = \infty$, $\Delta E = ?$, $\lambda = ?$

The corresponding initial and final energies are:

$$E_i = -\frac{21.79 \times 10^{-19}}{4} \text{ J} \quad \text{and} \quad E_f = \frac{21.79 \times 10^{-19}}{\infty} \text{ J}$$

$$= -5.45 \times 10^{-19} \text{ J} \qquad = 0$$

Therefore,

$$\Delta E = E_i - E_f = -5.45 \times 10^{-19} \text{ J} = -3.4 \text{ eV}$$

Further, we know that

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

or

$$\lambda = \frac{hc}{|\Delta E|}$$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{5.45 \times 10^{-19}}$$

$$= 3.649 \times 10^{-7}\ \text{m}$$

$$= 3649\ \text{Å}$$

Example 2.11 The energies of electron in the second and the third orbits of the hydrogen atom are -5.45×10^{-19} J and -2.41×10^{-19} J, respectively. Calculate the wavelength of the emitted radiation when the electron drops from the third orbit to the second orbit.

Solution: Given: $E_3 = -2.41 \times 10^{-19}$ J, $E_2 = -5.45 \times 10^{-19}$ J, $\lambda = ?$

Here, we know that $\Delta E = E_3 - E_2$

$$= -2.41 \times 10^{-19} + 5.45 \times 10^{-19}$$

$$= 3.04 \times 10^{-19}\ \text{J}$$

Further, $\Delta E = h\nu = \frac{hc}{\lambda}$

or $$\lambda = \frac{hc}{\Delta E}$$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{3.04 \times 10^{-19}}$$

$$= 6.538 \times 10^{-7}\ \text{m}$$

$$= 6538\ \text{Å}$$

Example 2.12 A single electron revolves around a stationary nucleus of charge + Ze, where Z is a constant and e is the magnitude of electronic charge. It requires 47.2 eV to excite the electron from the second Bohr orbit to the third Bohr orbit. Determine the following:

(i) The value of Z

(ii) The energy required to excite the electron from third Bohr orbit to the fourth Bohr orbit.

(iii) The wavelength of the electromagnetic radiation required to remove the electron from the first Bohr orbit to infinity.

(iv) The radius of the first Bohr orbit.

(v) The kinetic energy, the potential energy and the angular momentum of the electron in first Bohr orbit.

Solution: Given: $\Delta E = (E_3 - E_2) = 47.2$ eV

(i) We know that the energy of electron in n^{th} orbit around a stationary nucleus of change Ze (where Z is a constant) is given by

$$E_n = -\frac{Z^2 \times 13.6}{n^2}\ \text{eV}$$

so that

$$E_3 = -\frac{Z^2 \times 13.6}{9} \quad \text{and} \quad E_2 = -\frac{Z^2 \times 13.6}{4}$$

and $$E_3 - E_2 = Z^2 \times 13.6\left[\frac{1}{4} - \frac{1}{9}\right]$$

or $$47.2 = Z^2 \times 13.6 \times \frac{5}{36}$$

or $$Z^2 = \frac{47.2 \times 36}{13.6 \times 5} = 25$$

$\Rightarrow$ $$Z = 5$$

(ii) The energy required to excite the electron from $n = 3$ to $n = 4$ is given by

$$E_4 - E_3 = Z^2 \times 13.6\left[\frac{1}{9} - \frac{1}{16}\right]$$

$$= 25 \times 13.6\left[\frac{1}{9} - \frac{1}{16}\right]$$

$$= 25 \times 13.6 \times \frac{7}{144} = 16.53 \text{ eV}$$

(iii) The energy required to remove the electron from the first orbit to infinity is given by

$$E_\infty - E_1 = 25 \times 13.6\left[\frac{1}{1} - \frac{1}{\infty}\right] = 340 \text{ eV}$$

$$= 340 \times 1.6 \times 10^{-19} \text{ J}$$

$$= 544 \times 10^{-19} \text{ J}$$

Further, $$E_\infty - E_1 = \frac{hc}{\lambda}$$

or $$\lambda = \frac{hc}{E_\infty - E_1}$$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{544 \times 10^{-19}}$$

$$= 36.54 \times 10^{-10} \text{ m} = 36.54 \text{ Å}$$

(iv) We know that the radius of the n^{th} Bohr orbit is given by

$$r_n = \frac{n^2 h^2 \epsilon_0}{\pi m e^2 Z}$$

For first Bohr orbit, $n = 1$, so that

$$r_1 = \frac{h^2 \in_0}{\pi m e^2 Z}$$

or
$$r_1 = \frac{(6.626 \times 10^{-34})^2 \times 8.85 \times 10^{-12}}{3.14 \times 9.1 \times 10^{-31} \times (1.6 \times 10^{-19})^2 \times 5}$$

$$= 0.106 \times 10^{-10} \text{ m}$$

(v) The kinetic energy of the electron in the n^{th} orbit is given by

$$K.E = \frac{Ze^2}{8\pi \in_0 r_n}$$

For the first orbit, $n = 1$, so that

$$K.E = \frac{Ze^2}{2 \times 4\pi \in_0 r_1}$$

$$= \frac{5 \times (1.6 \times 10^{-19})^2 \times 9 \times 10^9}{2 \times (0.106 \times 10^{-10})^2}$$

$$= 512.64 \times 10^{-10} \text{ J}$$

Further, $P.E = -2 \times K.E = -2 \times 512.64 \times 10^{-10}$ J

$$= 1025.28 \times 10^{-10} \text{ J}$$

Angular momentum of the electron in the first Bohr orbit is given by

$$L_1 = mv_1 r_1 = \frac{h}{2\pi} = \frac{6.626 \times 10^{-34}}{2\pi}$$

$$= 1.05 \times 10^{-34} \text{ Js}$$

Example 2.13 Iodine molecule dissociates into two atoms after absorbing light of wavelength 4500 Å. If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atom (bond dissociation energy of $I_2 = 240$ kJ/mol.)

Solution: Given: $\lambda = 4500$ Å $= 4500 \times 10^{-10}$ m, bond dissociation energy of $I_2 = 240$ kJ/mol, $K.E$ of iodine atom = ?

Since energy used for breaking I_2 molecule

= Bond diss. energy of I_2

$= 240$ kJ/mol

$= 240 \times 10^3$ J/mol

$$= \frac{240 \times 10^3}{6.623 \times 10^{23}} \text{ J/molecule}$$

$= 3.984 \times 10^{-19}$ J/molecule

However, the energy absorbed by one I_2 molecule

$$= \frac{hc}{\lambda}$$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{4500 \times 10^{-10}}$$

$$= 4.417 \times 10^{-19} \text{ J/molecule}$$

Therefore, the amount of energy used in imparting $K.E$ to iodine molecule

$$= 4.417 \times 10^{-19} - 3.984 \times 10^{-19}$$

$$= 4.33 \times 10^{-20} \text{ J}$$

$\Rightarrow$ The energy used in imparting $K.E$ to each iodine atom

$$= \frac{4.33 \times 10^{-20}}{2} = 2.165 \times 10^{-20} \text{ J}$$

Example 2.14 Show that for large values of principal quantum number, the orbital frequency of electron in adjacent (consecutive) energy levels of hydrogen atom and the frequency of radiation for a transition between them have the same value.

Solution: Let us consider two consecutive energy levels (orbits) having principal quantum numbers n and $(n + 1)$, where $n >> 1$. Total energy by

$$E_n = -\frac{me^4Z^2}{8\epsilon_0^2 n^2 h^2} \quad \text{and} \quad E_{n+1} = -\frac{me^4Z^2}{8\epsilon_0^2 h^2 (n+1)^2}$$

For hydrogen atom $Z = 1$, therefore

$$(E_{n+1} - E_n) = \frac{me^4}{8\epsilon_0^2 h^2}\left[\frac{(n+1)^2 - n^2}{n^2(n+1)^2}\right]$$

$$= \frac{me^4}{8\epsilon_0^2 h^2}\left[\frac{n^2 + 1 + 2n - n^2}{n^2(n+1)^2}\right]$$

Since $n >> 1$, we obtain

$$(E_{n+1} - E_n) \simeq \frac{me^4}{8\epsilon_0^2 h^2}\left(\frac{2n}{n^4}\right)$$

$$= \frac{me^4}{4\epsilon_0^2 h^2 n^3}$$

If ν is the frequency of radiation for the transition between the two levels, then

$$h\nu_n = E_{n+1} - E_n = \frac{me^4}{4\epsilon_0^2 h^2 n^3}$$

or
$$\nu_n = \frac{me^4}{4\epsilon_0^2 h^3 n^3} \quad (1)$$

On the other hand, the orbital frequency of the electron in n^{th} orbit is given by

$$f_n = \frac{\text{Velocity of electron}}{\text{Orbital circumference}} = \frac{\nu_n}{2\pi r_n}$$

Substituting proper values of ν_n and r_n for hydrogen atom, we obtain

$$f_n = \frac{me^4}{4\epsilon_0^2 h^3 n^3} \quad (2)$$

Equation (1) and (2) are the same.

Example 2.15 The critical potential energy of hydrogen is 13.05 eV. Calculate the wavelength of the radiation emitted by hydrogen atom bombarded by an electron of corresponding energy.

Solution: Given: Critical potential of hydrogen atom

$$= 13.05 \text{ eV} = 13.05 \times 1.6 \times 10^{-19} \text{ J}, \lambda = ?$$

The wavelength corresponding to the critical potential energy is given by

$$13.05 \times 1.6 \times 10^{-19} = \frac{hc}{\lambda}$$

or
$$\lambda = \frac{hc}{13.05 \times 1.6 \times 10^{-19}}$$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{13.05 \times 1.6 \times 10^{-19}}$$

$$= 0.952 \times 10^{-7} \text{ m}$$

$$= 952 \text{ Å}$$

Example 2.16 Two lowest excited states of hydrogen atom are 10.2 eV and 12 eV above the ground state, calculate the wavelength of radiation that could be produced by transition between these states and the ground state.

Solution: Given: $n = 2$, $n = 3$ and $E_2 - E_1 = 10.2$ eV, $E_3 - E_1 = 12$ eV, $\lambda_1 = ?$, $\lambda_2, \lambda_3 = ?$

The wavelength (say λ_1) of the radiation corresponding to the transition from $n = 2$ to $n = 1$ state is given by

$$\frac{hc}{\lambda_1} = 10.2 \text{ eV}$$

or
$$\lambda_1 = \frac{hc}{10.2\ \text{eV}}$$
$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{10.2 \times 1.6 \times 10^{-19}\ \text{J}}$$
$$= 1.218 \times 10^{-7}\ \text{m}$$
$$= 1218\ \text{Å}$$

Similarly, the wavelength (say λ_2) of the radiation corresponding to the transition from n_3 to n_1 state is given by

$$\frac{hc}{\lambda_2} = 12\ \text{eV}$$

or
$$\lambda_2 = \frac{hc}{12\ \text{eV}}$$
$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{12 \times 1.6 \times 10^{-19}\ \text{J}}$$
$$= 1.035 \times 10^{-7}\ \text{m}$$
$$= 1035\ \text{Å}$$

Further, the energy difference between the two excited states is $E_3 - E_2 = 12 - 10.2 = 1.8$ eV

The wavelength (say λ_3) corresponding to this transition is

$$\frac{hc}{\lambda_3} = 1.8\ \text{eV}$$

or
$$\lambda_3 = \frac{hc}{1.8\ \text{eV}}$$
$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{1.8 \times 1.6 \times 10^{-19}\ \text{J}}$$
$$= 6.902 \times 10^{-7}\ \text{m}$$
$$= 6902\ \text{Å}$$

Example 2.17 The energy of a Bohr orbit is given by $\left(-\frac{B}{n^2}\right)$, where $B = 2.179 \times 10^{-18}$ J. Calculate the frequency of radiation and also the wave number, when the electron jumps from the third orbit to the second.

Solution: Given: $E_n = -\frac{B}{n^2}$ (where $B = 2.179 \times 10^{-18}$ J), $\nu = ?$, $\bar{\nu} = ?$

For the transition $n = 3$ to $n = 2$, we can write

$$E_2 = -\frac{B}{4} \quad \text{and} \quad E_3 = -\frac{B}{9}, \text{ therefore,}$$

$$\Delta E = E_3 - E_2 = -\frac{B}{9} + \frac{B}{4} = \frac{5B}{36} = h\nu$$

or

$$\nu = \frac{\Delta E}{h} = \frac{5B}{36h} = \frac{5 \times 2.179 \times 10^{-18}}{36 \times 6.626 \times 10^{-34}}$$

$$= 4.57 \times 10^{14}\ \text{s}^{-1}$$

Further,

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^8}{4.57 \times 10^{14}} = 6568\ \text{Å}$$

and

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{6568 \times 10^{-8}} = 1.52 \times 10^6\ \text{m}^{-1}$$

Example 2.18 In a Franck Hertz type experiment when atomic hydrogen is bombarded with electrons, excitation potentials of 10.21 eV and 12.10 eV are measured and the emission of three spectral lines is observed. Determine the wavelength and identify the spectral lines.

Solution: Given: Excitation potentials 10.21 eV and 12.10 eV, spectral lines = ?
wavelength = ?

For hydrogen atom, $Z = 1$ and the energy in the n^{th} orbit is given by

$$E_n = -\frac{B}{n^2} = -\frac{13.6}{n^2}$$

so that

$$E_1 = -\frac{13.6}{1} = -13.6\ \text{eV}$$

$$E_2 = -\frac{13.6}{4} = -3.4\ \text{eV}$$

and

$$E_3 = -\frac{13.6}{9} = 1.5$$

With the help of these energies one can check the energies required by the following transitions.

$K \rightarrow L$ requires energy, $\Delta E = E_2 - E_1 = -3.4 + 13.6 = 10.2$ eV
$K \rightarrow M$ requires energy, $\Delta E = E_3 - E_1 = -1.5 + 13.6 = 12.1$ eV
$L \rightarrow M$ requires energy, $\Delta E = E_3 - E_2 = -1.5 + 3.4 = 1.9$ eV

The wavelengths corresponding to these transitions are

$$\lambda_1 (K \rightarrow L) = \frac{hc}{10.2 \text{ eV}} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{10.2 \times 1.6 \times 10^{-19} \text{ J}}$$

$$= 1.218 \times 10^{-7} \text{ m}$$

$$= 1218 \text{ Å}$$

Similarly,

$$\lambda_2 (K \rightarrow M) = \frac{hc}{12.1 \text{ eV}} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{12.1 \times 1.6 \times 10^{-19} \text{ J}}$$

$$= 1.027 \times 10^{-7} \text{ m}$$

$$= 1027 \text{ Å}$$

Example 2.19 What electron energy must be supplied to the atoms of sodium vapour in order to stimulate the emission of sodium *D*-lines (where λ mean = 5893 Å)?

Solution: Given: λ mean = 5893 Å = 5893×10^{-10} m , ΔE = ?

The amount of energy supplied to the atom is

$$\Delta E = \frac{hc}{\lambda}$$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{5893 \times 10^{-10} \times 1.6 \times 10^{-19}}$$

$$= 2.11 \text{ eV}$$

Example 2.20 How much energy is required to raise the hydrogen atom from the ground state $n = 1$ to the first excited state $n = 2$? What is the wavelength of the line emitted if the atom returned to the ground from the excited state?

Solution: Given: Energy states $n = 1$ and $n = 2$, excitation energy = ? λ (emission) = ?

We know that the n^{th} state energy for hydrogen atom is given by

$$E_n = -\frac{13.6}{n^2} \text{ eV}$$

so that

$$E_1 = -\frac{13.6}{1} = -13.6 \text{ eV}$$

and

$$E_2 = -\frac{13.6}{4} = -3.4 \text{ eV}$$

Therefore, the required excitation energy is

$$\Delta E = E_2 - E_1$$

$$= -3.4 + 13.6 = 10.2 \text{ eV}$$

$$= 10.2 \times 1.6 \times 10^{-19} \text{ J}$$

$$= 16.32 \times 10^{-19} \text{ J}$$

The wavelength of the radiation corresponding to this transition ($n_2 \rightarrow n_1$) is

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{16.32 \times 10^{-19}}$$

$$= 1.218 \times 10^{-7} \text{ m}$$

$$= 1218 \text{ Å}$$

Example 2.21 What are the values of kinetic, potential and total energy of an electron in a hydrogen atom revolving in the first Bohr's orbit ($r_1 = 0.529$ Å) = ?

Solution: Given: $Z = 1, n = 1, r_1 = 0.529 \text{ Å} = 0.529 \times 10^{-10}$ m, $K.E = ?, P.E = ?,$ Total energy = ?

We know the kinetic energy of electron in the n^{th} orbit of hydrogen atom is given by

$$K.E = \frac{Ze^2}{8\pi\epsilon_0 r_n}$$

For $Z = 1, \quad n = 1$

$$K.E = \frac{e^2}{8\pi\epsilon_0 r_1}$$

$$= \frac{(1.6 \times 10^{-19})^2}{8 \times 3.14 \times 8.854 \times 10^{-12} \times 0.529 \times 10^{-10}}$$

$$= 2.17 \times 10^{-18} \text{ J}$$

$$= \frac{2.17 \times 10^{-18}}{1.6 \times 10^{-19}} \text{ eV} = 13.6 \text{ eV}$$

Further, the potential energy is numerically twice the $K.E.$

Therefore, $P.E = -2(K.E) = -2 \times 13.6 = -27.2$ eV

and total energy

$$E = K.E + P.E$$

$$= 13.6 - 27.2$$

$$= -13.6 \text{ eV}$$

Example 2.22 How many revolutions does an electron in the $n = 2$ state of a hydrogen atom make before dropping to $n = 1$ state? The average life time of an excited state is about 10^{-8} s).

Solution: Given: $n = 2$ state (of a hydrogen atom), $Z = 1$, average life time of an excited state $= 10^{-8}$ s, Number of revolutions made by an electron in $n = 2$ state before it drops to $n = 1$ state ?

We know that the radius of the n^{th} orbit is given by

$$r_n = \frac{n^2 h^2 \epsilon_0}{\pi m Z e^2}$$

Substituting the given values, we obtain

$$r_2 = \frac{4 \times (6.626 \times 10^{-34})^2 \times 8.854 \times 10^{-12}}{3.14 \times 9.1 \times 10^{-31} \times (1.6 \times 10^{-19})^2}$$

$$= 2.12 \times 10^{-10} \text{ m}$$

Therefore, the perimeter of the Bohr radius for $n = 2$ is

$$2\pi r_2 = 2\pi \times 2.12 \times 10^{-10}$$

$$= 13.32 \times 10^{-10} \text{ m}$$

Now, the velocity of electron in the n^{th} orbit is given by

$$v_n = \frac{Ze^2}{2hn\epsilon_0}$$

For $Z = 1$ and $n = 2$

$$v_2 = \frac{1 \times (1.6 \times 10^{-19})^2}{4 \times 6.626 \times 10^{-34} \times 8.854 \times 10^{-12}}$$

$$= 1.09 \times 10^6 \text{ ms}^{-1}$$

Thus the time for one revolution in $n = 2$ state is

$$t = \frac{2\pi r_2}{v_2}$$

$$= \frac{13.32 \times 10^{-10}}{1.09 \times 10^6} = 12.21 \times 10^{-16} \text{ s}$$

The number of revolutions in $n = 2$ state before fall is

$$n = \frac{\text{average life time in an orbit}}{\text{time for one revolution in the orbit}}$$

$$= \frac{10^{-8}}{12.21 \times 10^{-16}} = 8.19 \times 10^6$$

Example 2.23 Rubidium chloride assume CsCl structure at high pressure. Calculate the Rb – Cl distance in the CsCl structure from that of NaCl structure where the critical radius of the cation is 1.64 Å.

Solution: Given: RbCl assumes CsCl structure at high pressure, (R_X) critical = 1.64 Å. Rb – Cl distance = ?

We know that CsCl has a bcc strucutre and under critical condition (when all anions are in contact with the cations and also touch other anions). Thus

$R_M + R_X$ = half the body diagonal of the cube

$$= \frac{\sqrt{3}}{2} \text{ side of the cube}$$

$$= \frac{\sqrt{3}}{2} \times 2\, R_X = \sqrt{3}\, R_X$$

where $M \equiv$ Rb and $X \equiv$ Cl ions

Thus Rb – Cl bond distance $= R_M + R_X = \sqrt{3}\, R_X$

$$= \sqrt{3} \times 1.64$$

$$= 2.84 \text{ Å}$$

Example 2.24 Determine the radius of a cation having CsCl structure, when all anions are in contact with the cation and touch each other. The critical radius of the cation is 1.90 Å.

Solution: Given: The given strucutre is CsCl type, anions are in contact with the cations and touch each other, (R_X) critical = 1.90 Å, R_M = ?

For a CsCl type strucutre (under given condition) provides the relation

$$R_M + R_X = \sqrt{3}\, R_X$$

$$= \sqrt{3} \times 1.90$$

$$= 3.29 \text{ Å}$$

Therefore,

$$R_M = 3.29 - R_X$$

$$= 3.29 - 1.90$$

$$= 1.39 \text{ Å}$$

Example 2.25 In a CsCl structure (ρ = 3970 kg/m^3), the eight corners are occupied by Cl^- with Cs^+ at the center and vice-versa. Determine the distance between the neighbouring Cs^+ and Cl^- ions. If $r_{Cs^+} = 1.61$ Å, determine the radius ratio. Atomic masses of Cs = 132.91 and of Cl = 35.45.

Solution: Given: Crystal is *bcc*, $n = 1$ (molecule of CsCl) $\rho = 3970\ \text{kg/m}^3$, $M = 132.91 + 35.45 = 168.36$, $r_{Cs^+} = 1.61$ Å, $Cs^+ - Cl^-$ distance = ? r_{Cs^+}/r_{Cl^-} = ?

The volume of the unit call is given by

$$V = a^3 = \frac{M \times n}{\rho \times N}$$

$$= \frac{168.36 \times 1}{3970 \times 6.023 \times 10^{26}}$$

$$= 70.4 \times 10^{-30}\ \text{m}^3$$

$$\Rightarrow \quad a = 4.13 \times 10^{-10}\ \text{m}$$

$$= 4.13\ \text{Å}$$

Now, in a bcc unit call, we have

$$2(r_{Cs} + r_{Cl}) = \sqrt{3}\, a$$

or

$$r_{Cs} + r_{Cl} = \frac{\sqrt{3}}{2} a$$

$$= \frac{\sqrt{3} \times 4.13}{2}$$

$$= 3.57\ \text{Å}$$

This is the required Cs – Cl distance

Further, we have $r_{Cs^+} = 1.61$ Å and $r_{Cl^-} = 3.57 - 1.61 = 1.96$ Å

so that

$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{1.61}{1.96} = {}'0.82$$

Review Problems

2.1 Calculate for the hydrogen atom (a) velocity of the electron (b) radius of the orbit in the ground state (c) time taken by the electron to traverse the first Bohr orbit. *Ans.* 2.18×10^6 m/s, 0.529 Å, 1.52×10^{-16} s

2.2 How much energy is required to raise the hydrogen atom from the ground state ($n = 1$) to the first excited state ($n = 2$)? *Ans.* 10.2 eV

2.3 If the energy difference between two electron state is 46.12 k cal/mol. what will be the frequency of light emitted when the electrons drop from higher to lower states? (Given: $Nh = 9.52 \times 10^{-14}$ k cal/mol). *Ans.* 4.84×10^{14} cycles/s

2.4 Calculate the wavelength of the radiation that is emitted when an electron in orbit 2 returns to the orbit 1 in hydrogen atom. The ionization potential of the ground state of the hydrogen atom is 21.79×10^{-19} J/atom.

Ans. 1220 Å

2.5 The electron energy in hydrogen atom is given by

$$E_n = -\frac{21.79 \times 10^{-19}}{n} \text{ J}.$$

Calculate the energy required to remove an electron completely from the second orbit. What is the longest wavelength of light which causes this transition? *Ans.* -5.45×10^{-19} J, 3640 Å

2.6 An atom absorbs 5.2×10^{-18} J of energy. What will be the wavelength of the missing line in the spectrum of this atom? *Ans.* 382 Å

2.7 The energy of electron in the second and third Bohr orbit of hydrogen atom is -5.42×10^{-19} J and -2.41×10^{-19} J, respectively. Calculate the wavelength of the emitted radiation when the electron jumps from third to second orbit. *Ans.* 6608 Å

2.8 Calculate the frequency of the electron in the first Bohr orbit of hydrogen atom. *Ans.* 6.54×10^{15}/s

2.9 The electron energy in a hydrogen atom is given by $E = -\frac{B}{n^2}$, where $B = 2.179 \times 10^{-18}$ J. Calculate the frequency of radiation, wavelength and the wave number, when the electron jumps from the orbit $n = 3$ to $n = 2$. *Ans.* 4.56×10^{14} cycles/s, 6568 Å, 152×10^6 m^{-1}

2.10 The lowest two excited states of hydrogen atom are 10.2 eV and 12 eV above the ground state. Calculate the wavelength of radiation that could be produced by the transition between these states and the ground state. *Ans.* 1218 Å, 1035 Å and 6902 Å

MULTIPLE CHOICE QUESTIONS

2.1 In a hydrogen atom, radius of the first Bohr orbit is 0.53 Å, radius of the second Bohr orbit will be:

(a) 0.53 Å (b) 1.06 Å (c) 1.59 Å (d) 2.12 Å

2.2 For hydrogen atom, the first ionization patential is –13.6 eV, the second ionization potential will be:

(a) –13.6 eV (b) –27.2 eV (c) –6.8 eV (d) –3.4 eV

2.3 The minimum speed of the electrion revolving in the first Bohr orbit ($r_B = 0.53$ Å) of hydrogen atom such that it may not be pulled into the nucleus is:

(a) 1.18×10^6 m/s (b) 2.18×10^6 m/s
(c) 3.18×10^6 m/s (d) 4.18×10^6 m/s

2.4 The time taken by the electron in completing one revolution of the first Bohr orbit of hydrogen atom is:

(a) 1.53×10^{-16} s (b) 2.53×10^{-16} s
(c) 3.53×10^{-16} s (d) 4.53×10^{-16} s

2.5 Show that the number of waves made by a Bohr electron in one complete revolution in its second orbit is:

(a) 1 (b) 2 (c) 4 (d) 8

2.6 In a hydrogen atom, an electron in its ground state absorbs 1.5 times the minimum energy required for it to escape from the atom. The velocity associated with this is:

(a) 1.55×10^6 m/s (b) 2.55×10^6 m/s
(c) 3.55×10^6 m/s (d) 4.55×10^6 m/s

2.7 In a hydrogen atom, an electron in its ground state absorbs 1.5 times the minimum energy required for it to escape from the atom. The wavelength associated with this is:

(a) 1.7 Å (b) 2.7 Å (c) 3.7 Å (d) 4.7 Å

2.8 In a hydrogen atom, an electron jumps from the second orbit to the first orbit. The frequency of radiation emitted is:

(a) 1.46×10^{15} cycles/s (b) 2.46×10^{15} cycles/s
(c) 3.46×10^{15} cycles/s (d) 4.46×10^{15} cycles/s

2.9 In a hydrogen atom, an electron jumps from the second orbit to the first orbit. The wavelength of the radiation associated with this is:

(a) 1020 Å (b) 1120 Å (c) 1220 Å (d) 1320 Å

2.10 Electromagnetic radiation of wavelength 2420Å is just sufficient to ionize the sodium atom. The corresponding ionization energy is:

(a) 2.14 eV (b) 3.14 eV (c) 4.14 eV (d) 5.14 eV

2.11 In a hydrogen atom, the electron energy is the n^{th} Bohr's orbit is given by

$$E_n = \frac{-21.79 \times 10^{-19}}{n^2} \text{ J.}$$

The energy required to remove an electrion completely from the orbit $n = 2$ is:

(a) −1.4 eV (b) −2.4 eV (c) −3.4 eV (d) −4.4 eV

2.12 In a hydrogen atom, the electron energy in the n^{th} Bohr's orbit is given by

$$E_n = -\frac{21.79 \times 10^{-19}}{n^2} \text{ J.}$$

The wavelength associated with the electron in the orbit $n = 2$ is:

(a) 1649 Å (b) 2649 Å (c) 3649 Å (d) 4649 Å

2.13 In a hydrogen atom, the energy of electron in the second and third orbits are given by -5.45×10^{-19} J and -2.41×10^{-19} J, respectively. When the electron drops from the third orbit to the second orbit, the wavelength of the radiation emitted is:

(a) 4538 Å (b) 5538 Å (c) 6538 Å (d) 7538 Å

2.14 In a given atom, an electron revolves around the stationary nucleus. The energy required to excite the electron from the second orbit to the third orbit is 47.2 eV, the value of Z is:

(a) 4 (b) 5 (c) 6 (d) 7

2.15 Iodine molecule dissociates into two atoms after absorbing light of wavelength 4500 Å. The energy absorbed by each iodine atom is:

(a) 0.38 eV (b) 1.38 eV (c) 2.38 eV (d) 3.38 eV

2.16 In a hydrogen atom, the electron energy in the n^{th} Bohr's orbit is given by $-\frac{21.79 \times 10^{-19}}{n^2}$ J. When the electron jumps from the third orbit to the second orbit, the wave number associated with the electron is:

(a) $1.52 \times 10^6 \text{ m}^{-1}$ (b) $2.52 \times 10^6 \text{ m}^{-1}$
(c) $3.52 \times 10^6 \text{ m}^{-1}$ (d) $4.52 \times 10^6 \text{ m}^{-1}$

2.17 The energy supplied to the atoms of sodium vapour to stimulate the emission of sodium D line (where λ mean = 5893 Å) is:

(a) 0.11 eV (b) 1.11 eV (c) 2.11 eV (d) 3.11 eV

2.18 The energy required to raise the hydrogen atom from the ground state $n = 1$ to the first excited state $n = 2$ is:

(a) 4.32×10^{-19} J (b) 8.32×10^{-19} J
(c) 12.32×10^{-19} J (d) 16.32×10^{-19} J

2.19 In a hydrogen atom, the total energy of an electron revolving in the first Bohr orbit is:

(a) -13.6 eV (b) -11.6 eV (c) -9.6 eV (d) -7.6 eV

2.20 The angular momentum of the electron in the first Bohr's orbit is:

(a) 0.05×10^{-34} Js (b) 1.05×10^{-34} Js
(c) 2.05×10^{-34} Js (d) 3.05×10^{-34} Js.

ANSWERS

1. (d)	2. (d)	3. (b)	4. (a)	5. (b)	6. (a)	7. (d)
8. (b)	9. (c)	10. (d)	11. (c)	12. (c)	13. (c)	14. (b)
15. (b)	16. (a)	17. (c)	18. (d)	19. (a)	20. (b)	

CHAPTER 3

Atomic Bonding and Packing

Important Formulae

3.1 The potential energy of diatomic molecule in terms of interatomic distance R is given by

$$U(R) = -\frac{A}{R^n} + \frac{B}{R^m}$$

where A, B, m and n are constants characteristics of MX – molecule.
The force of interaction between the two atoms as a function of R is given by

$$F = -\frac{dU}{dR}$$

At equilibrium separation $R = R_e$, the attractive force is equal to the repulsive force and hence the net force acting on the atoms is zero, i.e.

$$F_{R=R_e} = -\left(\frac{dU}{dR}\right)_{R=R_e} = 0$$

The equilibrium separation can be found as

$$R_e = \left(\frac{mB}{nA}\right)^{\frac{1}{m-n}}$$

Similarly, the potential energy at equilibrium separation is obtained as

$$U_e = U_{R=R_e} = \frac{A}{R_e^n}\left(1 - \frac{n}{m}\right)$$

3.2 The potential energy of a diatomic molecule in terms of equilibrium separation R_e known as cohesive energy or lattice energy is given by

$$U_e = \frac{-Ae^2N}{4\pi\varepsilon_0 R_e}\left(1 - \frac{1}{n}\right) \text{ kJ/k mol.}$$

where A is the Madelung constant, N is the Avogadro's number. The repulsive exponent n is given by

$$n = 1 + \frac{72\pi\varepsilon_0 R_e^4}{K_0 A e^2} \quad \text{or} \quad \beta = \frac{A e^2 (n-1)}{72\pi\varepsilon_0 R_e^4}$$

where β is the Bulk modulus at absolute zero. This can also be defined as the reciprocal of compressibility, i.e.

$$\beta = \frac{1}{K_0}$$

3.3 For an exponential repulsion term in the potential energy equation, $U(R) = \dfrac{-AZ_1 Z_2 e^2}{4\pi\varepsilon_0 R} + B \exp\left(-\dfrac{R}{\rho}\right)$, the cohesive energy of an ionic solid can be written as

$$U_e = \frac{-Ae^2 N}{4\pi\varepsilon_0 R_e}\left(1 - \frac{\rho}{R_e}\right) \text{ kJ/k mol.}$$

where ρ is the repulsive exponent. This is given by

$$\frac{R_e}{\rho} = \frac{18R_e^4\,\beta}{Ae^2} + 2 \text{ and hence}$$

$$\frac{1}{K_0} = \beta = \frac{Ae^2}{18R_e^4}\left(\frac{R_e}{\rho} - 2\right)$$

3.4 Bond dissociation energy of ionic molecule is given by

$$D.E = -U_e - I.P + E.A.$$

where $I.P$ is the first ionization potential, $E.A.$ is the electron affinity.

3.5 The efficiency (also known as packing factor of filling factor) with which the available space is being filled is given by

$$\text{Efficiency} = \frac{\text{Volume of the atoms (in the unit cell)}}{\text{Volume of the unit cell}}$$

3.6 For an ideal close packing, the axial ratio c/a is given by

$$\frac{c}{a} = 0.8165 \times n$$

3.7 Size of the tetrahedral void is given by $r = 0.225\,R$, size of the octahedral void is given by $r = 0.414\,R$, where R is the radius of the close packed spheres.

Solved Examples

Example 3.1 The potential energy of a diatomic molecule in terms of interatomic distance R is given by

$$U(R) = -\frac{A}{R^m} + \frac{B}{R^n} \tag{1}$$

where A, B, m and n are constants characteristics for the MX – molecules.

(a) Derive an expression for the equilibrium spacing between the atoms.

(b) Explain the importance of equilibrium spacing as the configuration of lowest potential energy and hence obtain an expression for the dissociation energy of the atoms.

(c) Prove that $n > m$ for $U(R)$ to be minimum at $R = R_e$.

Solution: Given: The potential energy in the form of eq. 1, R_e = ?, U_e = ?, D = ? and show that $n > m$.

(a) Since at an equilibrium distance R_e (≡ bond length), the attractive and repulsive forces are equal, where the force of interaction between the two atoms as a function of R is given by

$$F = -\frac{dU}{dR}$$

$$= -\frac{mA}{R^{m+1}} + \frac{nB}{R^{n+1}} \quad \text{(from eq. 1)}$$

However, at an equilibrium distance ($R = R_e$), the net force acting on the atoms is zero. Therefore,

$$F = -\left(\frac{dU}{dR}\right)_{R=R_e} = 0 \tag{2}$$

$$\Rightarrow \quad \frac{mA}{R_e^{m+1}} = \frac{nB}{R_e^{n+1}}$$

Simplifying this for R_e, we obtain

$$R_e = \left(\frac{nB}{mA}\right)^{\frac{1}{n-m}} \tag{3}$$

This is the required expression for equilibrium separation.

(b) Substituting the value of R_e in eq. 1 and simplifying it, the corresponding equilibrium potential energy can be obtained, i.e.

$$U_e = U_{R=R_e} = -\frac{A}{R_e^m}\left(1 - \frac{m}{n}\right) \tag{4}$$

When the net force is zero, the potential energy is minimum and is negative. A positive quantity $D \equiv -U_e$ is called the dissociation energy of the molecule, i.e. the energy required to separate the two atoms.

(c) It is to be noted that the attractive and repulsive forces are equal at equilibrium separation, the attractive and repulsive energies are not because $m \neq n$. It is clear for eq. 4 that a minimum in the energy curve is possible only if $n > m$. Consequently, the formation of a chemical bond requires that the repulsive force must be of short range than the attractive ones. This may be shown readily by employing the condition that

$$\left(\frac{d^2U}{dR^2}\right)_{R=R_e} > 0$$

if U must have a minimum at R_e. This condition leads to

$$-\frac{m(m+1)A}{R_e^{m+2}} + \frac{n(n+1)B}{R_e^{n+2}} > 0$$

or $$n(n+1)B R_e^{m+2} - m(m+1)A R_e^{n+2} > 0$$

or $$n(n+1)B R_e^{m} > m(m+1)A R_e^{n}$$

or $$n(n+1)B > m(m+1)A R_e^{n-m}$$

Now substituting the values of R_e from eq. 3, we have

$$n(n+1)B > m(m+1)A \cdot \frac{nB}{mA}$$

or $$n+1 > m+1$$

or $$n > m$$

Example 3.2 Calculate the attractive force between a pair of Li^+ and Cl^- ions that just touch each other. Assume that the ionic radius of Li^+ ion to be 0.60 Å and that of Cl^- ion to be 1.81 Å.

Solution: Given: $r_{Li} = 0.60$ Å, $r_{Cl} = 1.81$ Å, $q_1 = q_2 = e = 1.6 \times 10^{-19}$ C, $F = ?$

As the ions touch each other, equilibrium separation between the two ions $r_e = 0.60 + 1.81 = 2.41$ Å $\times 10^{-10}$ m. The attractive force between the two ions is Coulombic,

$$F = \frac{1}{4\pi\varepsilon_0} \cdot \frac{q_1 q_2}{r_e^2}$$

Substituting different values, we obtain

$$F = \frac{9 \times 10^9 \times (1.6 \times 10^{-19})^2}{(2.41 \times 10^{-10})^2}$$

$$= 3.96 \times 10^{-9} \text{ N}$$

Example 3.3 The potential energy of a system of two atoms is given by

$$U(R) = -\frac{\alpha}{R^4} + \frac{\beta}{R^{12}} \quad (1)$$

Calculate the amount of energy released when the atoms form a stable bond. Determine the bond length.

Solution: Given: The potential energy in the form of eq. 1, $U_e = ?\ R_e = ?$

We know that the force of interaction between the two atoms is given by

$$F = -\frac{dU}{dR} \quad (2)$$

$$= -\frac{4\alpha}{R^5} + \frac{12\beta}{R^{13}}$$

However, at an equilibrium distance (≡ bond length) $R = R_e$, the net force acting on the atoms is zero. Therefore,

$$F = -\left(\frac{dU}{dR}\right)_{R=R_e} = 0 \quad (3)$$

$$\Rightarrow \qquad \frac{4\alpha}{R_e^5} = \frac{12\beta}{R_e^{13}}$$

$$\text{or} \qquad R_e^8 = \frac{12\beta}{4\alpha} = \frac{3\beta}{\alpha}$$

$$\text{or} \qquad R_e = \left(\frac{3\beta}{\alpha}\right)^{1/8} \quad (4)$$

This is the required bond length. Now substituting the value of R_e in eq. 1 for R and simplifying it, we obtain the amount of energy released, i.e.

$$U_e = -\frac{\alpha}{R_e^4}\left(1 - \frac{1}{3}\right)$$

$$= -\frac{\alpha}{\left(\frac{3\beta}{\alpha}\right)^{1/2}} \times \frac{2}{3} = -\left(\frac{4\alpha^3}{27\beta}\right)^{1/2}$$

This is the required energy when the atoms form a stable bond.

Example 3.4 The potential energy of a system of two atoms is given by (1)

$$U = -\frac{A}{R^6} + \frac{B}{R^{12}}$$

The atoms form a stable bond with bond length of 3 Å and bond energy of 1.8 eV. Calculate A, B, the force required to break the molecule and the critical interatomic distance for which it occurs.

Solution: Given: $R_e = 3\ \text{Å} = 3 \times 10^{-10}$ m, $D = -U_e = 1.8$ eV $= 1.8 \times 1.6 \times 10^{-19}$ J, $m = 6, n = 12, A = ?, B = ?, R_e = ?, F_c = ?$

Making use of the equation for dissociation energy, we have

$$D = -U_e = \frac{A}{R_e^m}\left(1 - \frac{m}{n}\right)$$

Substituting different values and simplifying for A, we obtain

$$A = 2DR_e^6$$

$$= 2 \times 1.8 \times 1.6 \times 10^{-19} \times (3 \times 10^{-10})^6$$

$$= 4.19 \times 10^{-76}\ \text{Jm}^6$$

Further, we know that at equilibrium separation, the net force is zero, i.e.

$$F = -\left(\frac{dU}{dR}\right)_{R=R_e} = -\frac{6A}{R_e^7} + \frac{12B}{R_e^{13}} = 0$$

This gives us,

$$B = \frac{A(R_e)^6}{2}$$

$$= \frac{4.19 \times 10^{-76} \times (3 \times 10^{-10})^6}{2}$$

$$= 1.53 \times 10^{-133}\ \text{Jm}^{12}$$

Further, we know that $F(R) = -\dfrac{dU}{dR} = 0$ will be minimum or maximum when $\dfrac{dF}{dR} = 0$ and $R = R_c$ (called the critical separation). Thus

$$\left(\frac{dF}{dR}\right)_{R=R_c} = \left(\frac{d^2U}{dR^2}\right)_{R=R_c} = \frac{42A}{R_c^8} - \frac{156\,B}{R_c^{14}} = 0$$

Substituting the value of B/A from above and simplifying this, we obtain

$$R_c^6 = \frac{13}{7} R_e^6$$

or

$$R_c = \left(\frac{13}{7}\right)^{1/6} R_e$$

$$= \left(\frac{13}{7}\right)^{1/6} \times 3 \times 10^{-10}$$

$$= 3.33 \times 10^{-10}\ m = 3.33\ \text{Å}$$

Now, the minimum force required to break the bond at $R = R_c$ is given by

$$F_{min} = -\left(\frac{dU}{dR}\right)_{R=R_c}$$

$$= -\frac{6A}{R_c^7} + \frac{12B}{R_c^{13}}$$

$$= -\frac{6A}{R_c^7}\left(1 - \frac{2B}{AR_c^6}\right)$$

$$= -\frac{6A}{R_c^7}\left[1 - \left(\frac{R_e}{R_c}\right)^6\right]\left(\because \frac{B}{A} = \frac{R_e^6}{2}\right)$$

$$= -\frac{6 \times 4.19 \times 10^{-76}}{(3.33 \times 10^{-10})^7}\left[1 - \left(\frac{3}{3.33}\right)^6\right]$$

$$= -2.58 \times 10^{-9}\ \text{N}$$

The negative sign indicates that the force at $R = R_c$ is attractive in nature. Thus the force needed to dissociate the molecule is 2.58×10^{-9} N.

Example 3.5 The potential energy of a diatomic molecule in terms of interatomic distance R is given by

$$U(R) = -\frac{A}{R^2} + \frac{B}{R^{10}} \tag{1}$$

Calculate (i) the equilibrium separation and the dissociation energy when $A = 1.44 \times 10^{-39}$ Jm^2 and $B = 2.19 \times 10^{-115}$ Jm^{10}.
(ii) A', B' and the force required to break the molecule and the critical distance between the nuclei for which this occurs when the two atoms form a stable molecule with an internuclear distance of 3 Å and the dissociation energy 4 eV.

Solution: Given: The potential energy in the form of eq.1, $m = 2$, $n = 10$.

(i) $A = 1.44 \times 10^{-39}$ Jm^2, $B = 2.19 \times 10^{-115}$ Jm^{10}, $R_e = ?$, $D = ?$

(ii) $R_e' = 3$ Å $= 3 \times 10^{-10}$ m, $D' = 4$ eV, $A' = ?$, $B' = ?$ $R_c = ?$ $F_{min} = ?$

(i) Making use of the equation for equilibrium separation,

$$R_e = \left(\frac{nB}{mA}\right)^{\frac{1}{n-m}} \tag{2}$$

and substituting different values, we have

$$R_e = \left(\frac{10 \times 2.19 \times 10^{-115}}{2 \times 1.44 \times 10^{-39}}\right)^{\frac{1}{8}}$$

$$= (76042 \times 10^{-80})^{\frac{1}{8}}$$

$$= 4.08 \times 10^{-10}\ \text{m} = 4.08\ \text{Å}$$

Further, to obtain the dissociation energy, we use the equation,

$$D = -U_e = \frac{A}{R_e^m}\left(1 - \frac{m}{n}\right) \quad (3)$$

Substituting different values, we obtain

$$D = \frac{4A}{5R_e^2}$$

$$= \frac{4 \times 1.44 \times 10^{-39}}{5 \times (4.08 \times 10^{-8})^2} \text{ in Joules}$$

$$= \frac{4 \times 1.44 \times 10^{-39}}{5 \times (4.08 \times 10^{-10})^2 \times 1.6 \times 10^{-19}} \text{ in eV}$$

$$= 4.33 \times 10^{-2} \text{ eV}$$

(ii) Now, substituting the given values of n and m in eq. 3, we obtain

$$A' = \frac{5R_e^2 \times D}{4}$$

$$= \frac{5 \times (3 \times 10^{-10})^2 \times 4 \times 1.6 \times 10^{-19}}{4}$$

$$= 7.2 \times 10^{-38} \text{ Jm}^2$$

Similarly, substituting the values of A' and the given value of R_e' in Eq. 2 we obtain

$$B' = \frac{A \times (R_e)^8}{5}$$

$$= \frac{7.2 \times 10^{-38} \times (3 \times 10^{-10})^8}{5}$$

$$= 9.45 \times 10^{-115} \text{ Jm}^{10}$$

In order to obtain R_c, let us apply the condition

$$\left(\frac{dF}{dR}\right)_{R=R_c} = \left(\frac{d^2U}{dR^2}\right)_{R=R_c} = \frac{6A}{R_c^4} - \frac{110B}{R_c^{12}} = 0$$

Substituting the value of $B'/A' = (R_e')^8/5$ from above and simplifying this, we have

$$R_c = \left(\frac{11}{3}\right)^{\frac{1}{8}} \times R_e' = \left(\frac{11}{3}\right)^{\frac{1}{8}} \times 3 \times 10^{-10} = 3.53 \text{ Å}$$

Now the minimum force at $R = R_c$ is given by

$$F_{min} = -\left(\frac{dU}{dR}\right)_{R=R_c} = -\frac{2A}{R_c^3} + \frac{10B}{R_c^{11}} = -\frac{2A}{R_c^3}\left(1 - \frac{10B}{2AR_c^8}\right)$$

Substituting the value of $B'/A' = (R_e')^8/5$ and simplifying, we have

$$F_{min} = -\frac{2A}{R_c^3}\left[1 - \left(\frac{R_e}{R_c}\right)^8\right]$$

$$= -\frac{2 \times 7.2 \times 10^{-38}}{(3.53 \times 10^{-10})^3}\left[1 - \left(\frac{3}{3.53}\right)^8\right]$$

$$= -2.38 \times 10^{-9} \text{ J/m}$$

$$= -2.38 \times 10^{-9} \text{ N}$$

The negative sign indicates that the forces at $R \doteq R_c$ is attractive in nature. Thus the force needed to dissociate the molecule is 2.38×10^{-9} N.

Example 3.6 Show that the Madelung constant A for an infinite linear chain of ions of alternating charge at an equilibrium separation is 2ln2.

Solution: Madelung constant A is a function of crystal structure and can therefore be calculated from the geometrical arrangement of ions in a crystal.

In the present case, we have to calculate the Madelung constant for an infinite linear chain of ions of alternating charge (i.e. a one dimensional NaCl crystal) at equilibrium separation R_e (Fig. 3.1). Let us take one sodium ion as the reference ion and then write various terms of the series for alternating ions in terms of R_e, we obtain

$$A = 2\left(\frac{1}{1} - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \ldots\right)$$

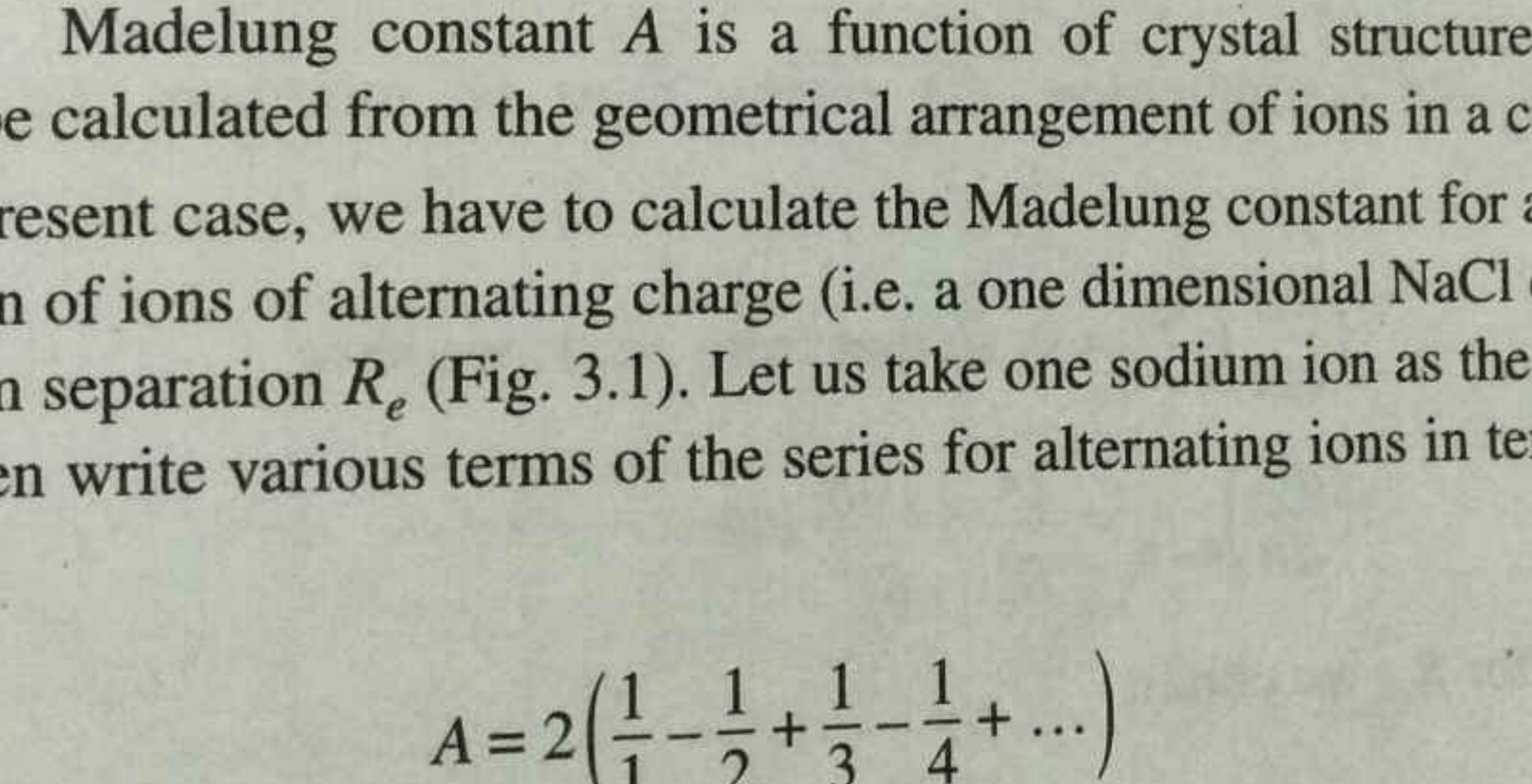


Fig. 3.1 Geometry of a one dimensional NaCl crystal

Making use of the series

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \ldots \text{ with } x = 1,$$

we obtain

$$A = 2\ln 2$$

$$= 1.3863$$

Example 3.7 Show that the potential energy of two particles in stable configuration (at equilibrium) is equal to $-\frac{4}{5}\left(\frac{A}{R_e^2}\right)$ for $m = 2$ and $n = 10$.

Solution: Given: $m = 2$, $n = 10$, prove that $U = -\frac{4}{5}\left(\frac{A}{R_e^2}\right)$ at equilibrium separation.

The general form of the potential energy equation for a diatomic molecule in terms of interatomic distance R is given by

$$U(R) = -\frac{A}{R^m} + \frac{B}{R^n}$$

$$= -\frac{A}{R^2} + \frac{B}{R^{10}} \qquad \text{(1) for } m = 2 \text{ and } n = 10$$

For a stable configuration, the energy must be minimum, i.e. $U_{R=R_e}$ = minimum

$\Rightarrow$ $\left(\frac{dU}{dR}\right)_{R=R_e} = 0$, so that from eq. 1, we have

$$\left(\frac{dU}{dR}\right)_{R=R_e} = \frac{2A}{R_e^3} - \frac{10B}{R_e^{11}} = 0$$

Solving for R_e, we obtain

$$R_e = \left(\frac{5B}{A}\right)^{1/8} \qquad (2)$$

Substituting this value for R in eq. 1, we obtain

$$U_{R=R_e} = -\frac{A}{\left(\frac{5B}{A}\right)^{1/4}} + \frac{B}{\left(\frac{5B}{A}\right)^{5/4}}$$

$$= -A \times \left(\frac{A}{5B}\right)^{1/4}\left[1 - \frac{1}{5}\right]$$

$$= -\frac{4A}{5} \times \frac{1}{R_e^2} = -\frac{4}{5}\left(\frac{A}{R_e^2}\right) \text{ Proved}$$

Example 3.8 What is the potential energy of CsCl at equilibrium, if the separation between cesium and chlorine atoms is 3.56 Å, $A = 1.76$ and n is 11.5?

Solution: Given: $R_e = 3.56\ \text{Å} = 3.56 \times 10^{-10}$ m, $n = 11.5$, $A = 1.76$, $U_e = ?$

We know that the potential energy per ion pair is given by

$$U_e = -\frac{Ae}{4\pi\in_0 R_e}\left(1-\frac{1}{n}\right) \text{ in eV} = -\frac{Ae^2}{4\pi\in_0 R_e}\left(1-\frac{1}{n}\right) \text{ in Joules}$$

$$= -\frac{1.76 \times 1.6 \times 10^{-19} \times 9 \times 10^9}{3.56 \times 10^{-10}} \times \frac{10.5}{11.5} \text{ eV}$$

$$= -6.50 \text{ eV}$$

Example 3.9 Calculate the Madelung constant for an infinite array of two – dimensional ionic charge distribution (i.e. two dimensional NaCl crystal) with equilibrium ion separation as R_e.

Solution: Consider a two dimensional array of ionic charge (alternate Na^+ and Cl^- ion) distribution as shown as Fig. 3.2. Let us take Na^+ ion (at left bottom corner) as the reference ion and then write various term of the series for alternating ions in term of increasing value of R_e, we have

$$A = 4\left[\left(\frac{1}{1}-\frac{1}{\sqrt{2}}\right)+\left(\frac{1}{\sqrt{4}}+\frac{2}{\sqrt{5}}-\frac{1}{\sqrt{8}}\right)+\left(\frac{1}{3}-\frac{2}{\sqrt{10}}+\frac{2}{\sqrt{13}}-\frac{1}{\sqrt{18}}\right)\right.$$

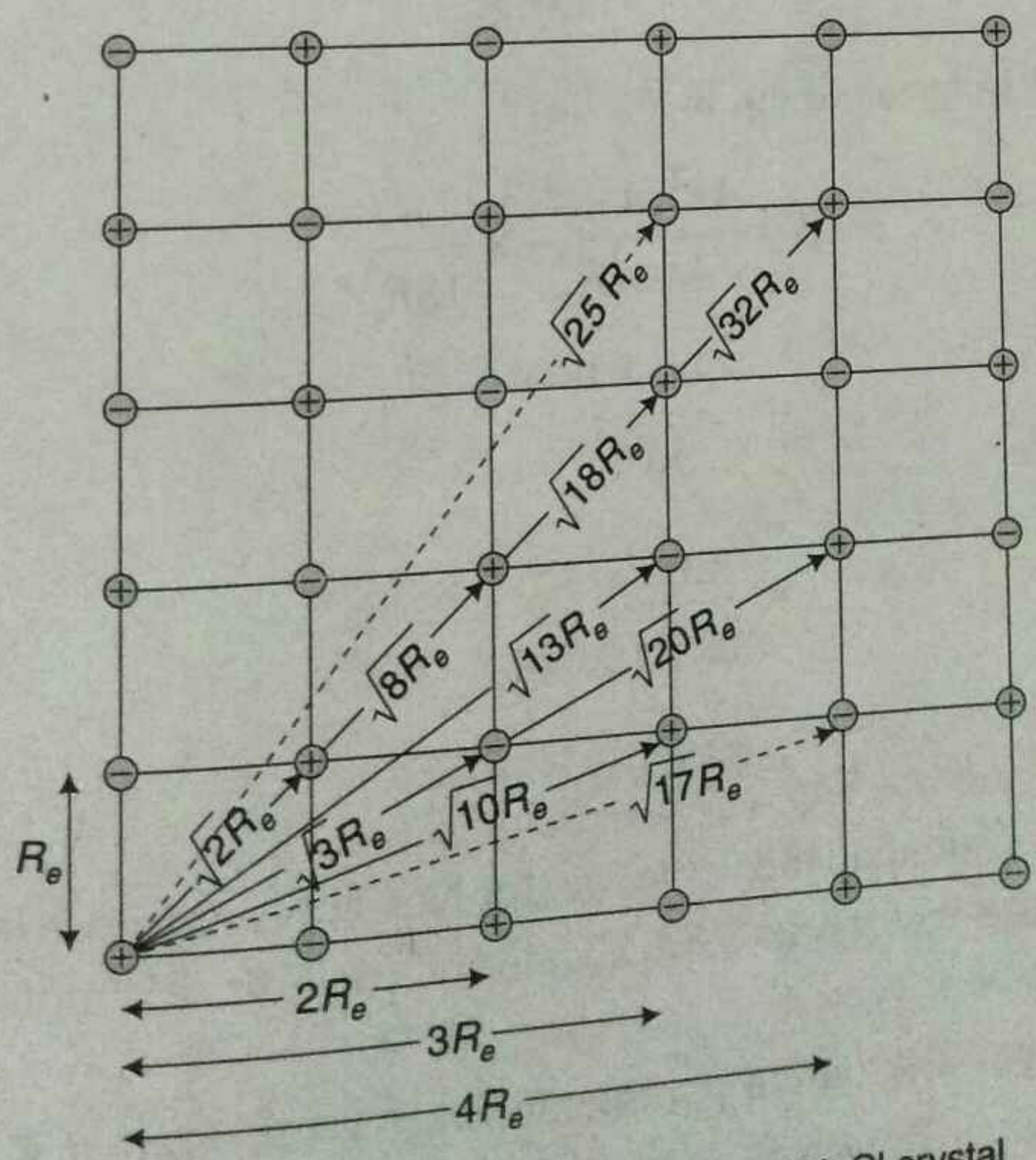


Fig. 3.2 Geometry of two – dimensional NaCl crystal

$$+\left(-\frac{1}{\sqrt{16}}+\frac{2}{\sqrt{17}}-\frac{2}{\sqrt{20}}+\frac{2}{\sqrt{25}}-\frac{1}{\sqrt{32}}\right)+\cdots\Bigg]$$

$$=1.1716+0.1635+0.0795+0.0443+\cdots$$

$$\simeq 1.6135$$

Example 3.10 The cohesive energy and the nearest neighbour distance for an *LiF* molecule are -1.68×10^{-18} J and 2.014 Å, respectively. The structure of *LiF* is the same as that of NaCl with $n = 6.26$. Calculate the bulk modulus of *LiF* using the potential energy equation:

$$U=-\frac{Ae^2}{R}+\frac{B}{R^n} \tag{1}$$

where A is the Madelung constant and is equal to 1.75.

Solution: Given: Cohesive energy, $U_e = -1.68\times10^{-18}$ J, $R_e = 2.014$ Å $= 2.014\times10^{-10}$ m, $n = 6.26$, $\beta = ?$

For the given potential, the cohesive energy is given by

$$U_e=-\frac{Ae^2}{4\pi\in_0 R_e}\left(1-\frac{1}{n}\right)=-\frac{Ae^2}{4\pi\in_0 R_e}\left(\frac{n-1}{n}\right) \tag{2}$$

We also know that the Bulk modulus is given by

$$\frac{1}{K_0}=\beta=\frac{Ae^2(n-1)}{72\pi\in_0 R_e^4} \tag{3}$$

Writing eq. 3 in terms of eq. 2, we have

$$\beta=\frac{Ae^2(n-1)}{4\pi\in_0 R_e^n}\times\frac{n}{18R_e^3}$$

$$=-\frac{U_e\times n}{18R_e^3}$$

$$=\frac{1.68\times10^{-18}\times6.26}{18\times(2.014\times10^{-10})^3}$$

$$=7.15\times10^{10}\ \mathrm{Nm^{-2}}$$

Example 3.11 Calculate the value of n for NaCl crystal whose lattice parameter is 5.63 Å, binding energy is 1.83 k cal/mol (or 7.95 eV/molecule) and A is 1.75, respectively.

Solution: Given: The lattice parameter, $a = 5.63$ Å, so that $R_e = \frac{5.63}{2} = 2.81$ Å $= 2.81\times10^{-10}$ m, $A = 1.75$, $B.E = 1.83$ k cal/mol $= 7.95$ eV/molecule. $n = ?$

We know that the binding energy is the equilibrium potential energy per ion pair in magnitude. This is given by

$$B.E = \frac{Ae}{4\pi\in_0 R_e}\left(1-\frac{1}{n}\right) \text{ in eV} = \frac{Ae^2}{4\pi\in_0 R_e}\left(1-\frac{1}{n}\right) \text{ in Joules}$$

Substituting different values, we obtain

$$\left(1-\frac{1}{n}\right) = \frac{B.E \times 4\pi\in_0 \times R_e}{Ae}$$

$$= \frac{7.95 \times 2.81 \times 10^{-10}}{1.75 \times 9 \times 10^9 \times 1.6 \times 10^{-19}}$$

$$= 0.89$$

or
$$\frac{1}{n} = 1 - 0.89 = 0.11$$

or
$$n = 9$$

Example 3.12 Calculate the compressibility of sodium chloride by assuming a repulsive potential of the form B/R^9 to act between the nearest neighbours. The nearest neighbour distance R_e = 2.81 Å and the corresponding Madelung constant A = 1.7476.

Solution: Given: $R_e = 2.81$ Å $= 2.81 \times 10^{-10}$ m, $A = 1.7476$, $n = 9$, $K_0 = ?$

The compressibility of NaCl can be calculated by using the equation

$$K_0 = \frac{72\pi\in_0 R_e^4}{(n-1)Ae^2}$$

$$= \frac{18 \times 4\pi\in_0 R_e^4}{(n-1)Ae^2}$$

Substituting different values, we obtain

$$K_0 = \frac{18 \times (2.81 \times 10^{-10})^4}{8 \times 1.7476 \times 9 \times 10^9 \times (1.6 \times 10^{-19})^2}$$

$$= 3.48 \times 10^{-11} \text{ m}^2\text{N}$$

Example 3.13 If an atom A has an ionization energy 5 eV, another atom B has an electron affinity 4 eV and they are 5 Å apart, calculate the energy required to transfer an electron form A to B.

Solution: Given: Ionization potential energy of atom A = 5 eV, electron affinity of atom B = 4 eV, equilibrium separation $R_e = 5$ Å $= 5 \times 10^{-10}$ m, energy to transfer an electron from A to B = ?

The potential energy of a pair of atoms in AB system is

$$U = -\frac{e}{4\pi\in_0 R_e} \text{ in eV} = -\frac{e^2}{4\pi\in_0 R_e} \text{ in Joules}$$

Substituting different values, we get

$$U = -\frac{1.6 \times 10^{-19} \times 9 \times 10^9}{5 \times 10^{-10}}$$

$$= -2.88 \text{ eV}$$

Now, the energy required to transfer an electron from A to B is

$$E_r = \Delta U + U$$

$$= I.P - E.A + U$$

$$= 5 - 4 - 2.88$$

$$= -1.88 \text{ eV}$$

Example 3.14 The ionization potential energy of K (potassium) is 4.1 eV and the electron affinity of Cl (chlorine) is 3.6 eV. Determine (i), the energy required to form a K^+ and Cl^- ion pair from a pair of K and Cl atoms (ii) separation between K^+ and Cl^- ion pair if their total energy is to be zero.

Solution: Given: $I.P$ (of K) = 4.1 eV, $E.A$ (of Cl) = 3.6 eV, E_r to form K^+ and Cl^- ion pair = ?, R_e = ?

We know that the net energy required to form an ion pair is

$$E_r = \Delta E = I.P - E.A = 4.1 - 3.6 = 0.5 \text{ eV}$$

Now, if their total energy is to be zero, then $E_r = E_c$ (the Coulomb energy). Therefore,

$$E_c = 0.5 = -\frac{e}{4\pi\in_0 R_e} \text{ in eV}$$

or

$$R_e = -\frac{1.6 \times 10^{-19} \times 9 \times 10^9}{0.5} = 28.8 \times 10^{-10} \text{ m} = 28.8 \text{ Å}$$

Example 3.15 Calculate the cohesive energy per ion of NaCl molecule from the following data: $A = 1.748$, $n = 9$, $R_e = 2.81$ Å, ionization potential energy of Na = 5.14 eV and electron affinity of Cl = 3.61 eV.

Solution: Given: $A = 1.748$, $n = 9$, $R_e = 2.81$ Å $= 2.81 \times 10^{-10}$ m, I.P. of Na = 5.14 eV, $E.A$ of Cl = 3.61 eV, cohesive energy = ?

The cohesive energy per ion pair is given by

$$U = -\frac{Ae}{4\pi\in_0 R_e}\left(1 - \frac{1}{n}\right) \text{ in eV} = -\frac{Ae^2}{4\pi\in_0 R_e}\left(1 - \frac{1}{n}\right) \text{ in Joules}$$

$$= \frac{1.748 \times 1.6 \times 10^{-19} \times 9 \times 10^{9} \times 8}{2.81 \times 10^{-10} \times 9}$$

$$= 7.96 \text{ eV}$$

Therefore, the potential energy per ion = 3.98 eV. Further, the energy required to produce the ion pair is

$$\Delta E = I.P - E.A = 5.14 - 3.61 = 1.53 \text{ eV}$$

Therefore the energy contribution per ion = 1.536/2 = 0.76 eV

Hence, the cohesive energy per ion (atom) is

$$-3.98 + 0.76 = -3.22 \text{ eV}$$

Example 3.16 Assuming an overlap interaction between the nearest neighbours of exponential type $U(R) = B \exp(-R/\rho)$, where B and ρ are constants, show that the equilibrium spacing is given by $R_e = \rho \ln B$.

Solution: Given: $U(R) = B \exp(-R/\rho)$

At equilibrium spacing $R = R_e$, $U(R = R_e) = 0$

so that $B \exp(-R_e/\rho) = 0$

or $$\ln B - \frac{R_e}{\rho} = 0$$

or $$\frac{R_e}{\rho} = \ln B$$

or $$R_e = \rho \ln B$$

Example 3.17 Calculate the cohesive energy of NaCl if the Madelung constant is 1.748, the equilibrium NaCl bond distance is 2.81 Å and the repulsion exponent is 0.32 Å.

Solution: Given: $A = 1.748$, $R_e = 2.81$ Å $= 2.81 \times 10^{-10}$ m, $\rho = 0.32$ Å $= 0.32 \times 10^{-10}$ m, cohesive energy = ?

Making use of the formula of the cohesive energy per ion pair containing the repulsion exponent, we have

$$U = \frac{Ae}{4\pi \in_0 R_e}\left(1 - \frac{\rho}{R_e}\right) \text{ in eV}$$

or $$U = -\frac{1.748 \times 1.6 \times 10^{-19} \times 9 \times 10^{9}}{2.81 \times 10^{-10}}\left(1 - \frac{0.32 \times 10^{-10}}{2.81 \times 10^{-10}}\right)$$

$$= -\frac{1.748 \times 1.6 \times 10^{-19} \times 9 \times 10^{9} \times 0.886}{2.81 \times 10^{-10}}$$

$$= -7.94 \text{ eV}$$

Example 3.18 Determine the cohesive energy per atom (ion) and hence the dissociation energy per atom (ion) for KCl if the ionization potential of potassium is 4.11 eV and the electron affinity of chlorine is 3.61 eV. The Madelung constant of KCl is 1.75, the nearest neighbour separation is 3.14 Å and the volume of repulsive constant is 5.77.

Solution: Given: $I.P$ (of K) = 4.11 eV, $E.A$ (of Cl) = 3.61 eV, $A = 1.75$, $R_e = 3.14$ Å $= 3.14 \times 10^{-10}$ m, $n = 5.77$

The cohesive energy per ion – pair is given by

$$U = -\frac{Ae}{4\pi\epsilon_0 R_e}\left(1-\frac{1}{n}\right) \text{ in eV} = -\frac{Ae^2}{4\pi\epsilon_0 R_e}\left(1-\frac{1}{n}\right) \text{ in Joules}$$

$$= -\frac{1.75 \times 1.6 \times 10^{-19} \times 9 \times 10^9 \times 4.77}{5.77 \times 3.14 \times 10^{-10}}$$

$$= -6.63 \text{ eV}$$

Hence, the potential energy per ion = – 3.32 eV. Further, the energy required to produce the ion pair is

$$\Delta E = I.P - E.A = 4.11 - 3.61 = 0.50 \text{ eV}$$

so that the contribution per ion = 0.50/2 = 0.25 eV.

Hence, the cohesive energy per ion (atom) is

$$-3.32 + 0.25 = -3.07 \text{ eV}$$

Thus the dissociation energy per ion is $D = -U = 3.07$ eV

Example 3.19 For NaCl the Madelung constant $A = 1.75$, the cohesive energy is 6.61 eV, interatomic separation is 2.82 Å, the ionization energy of Na is 5.138 eV and the electron affinity is 3.61 eV. If the repulsive energy is of the form $B \exp\left(-\frac{R}{\rho}\right)$, determine the values of B and ρ?

Solution: Given: Madelung constant $A = 1.75$, cohesive energy per ion pair 6.61 eV, $R_e = 2.82$ Å $= 2.82 \times 10^{-10}$ m, $I.P = 5.138$ eV, $E.A = 3.61$ eV, $B = ?$, $\rho = ?$

We know that the potential energy of NaCl ion pair in the exponential form at equilibrium separation is

$$U_e = -\frac{Ae^2}{4\pi\epsilon_0 R_e} + B \exp\left(-\frac{R_e}{\rho}\right) \quad (1)$$

and the cohesive energy per ion pair becomes

$$-6.61 = U_e + I.P - E.A \quad (2)$$

or

$$U_e = -6.61 - 5.138 + 3.61 = -8.138$$

Differentiating eq. 1 and at $R = R_e$ we obtain

$$\left(\frac{dU_e}{dR}\right)_{R=R_e} = \frac{Ae^2}{4\pi\in_0 R_e^2} - \frac{B}{\rho}\exp\left(-\frac{R_e}{\rho}\right) = 0$$

or
$$\frac{B}{\rho}\exp\left(-\frac{R_e}{\rho}\right) = \frac{Ae^2}{4\pi\in_0 R_e^2}$$

or
$$B\exp\left(-\frac{R_e}{\rho}\right) = \frac{\rho Ae^2}{4\pi\in_0 R_e^2}$$

Substituting this in eq. 1, we obtain

$$U_e = -\frac{Ae^2}{4\pi\in_0 R_e} + \rho\frac{Ae^2}{4\pi\in_0 R_e^2} \text{ in Joules}$$

$$= -\frac{Ae}{4\pi\in_0 R_e} + \rho\frac{Ae}{4\pi\in_0 R_e^2} \text{ in eV}$$

Substituting the value of U_e from eq. 2, we obtain

$$-8.138 = -\frac{Ae}{4\pi\in_0 R_e} + \rho\frac{Ae}{4\pi\in_0 R_e^2}$$

or
$$-8.138 = \frac{Ae}{4\pi\in_0 R_e}\left(1 - \frac{\rho}{R_e}\right)$$

$$= -\frac{1.75 \times 1.6 \times 10^{-19} \times 9 \times 10^9}{2.82 \times 10^{-10}}\left(1 - \frac{\rho}{2.82 \times 10^{-10}}\right)$$

$$= -8.936\left(1 - \frac{\rho}{2.82 \times 10^{-10}}\right)$$

Solving for ρ, we obtain

$$\rho = 0.25 \times 10^{-10} \text{ m} = 0.25 \text{ Å}$$

Substituting the value of ρ in eq. 1 and solving for B, we obtain

$$-8.138 = -\frac{Ae}{4\pi\in_0 R_e} \text{ (in eV)} + B\exp\left(-\frac{R_e}{\rho}\right)$$

or
$$B\exp\left(-\frac{R_e}{\rho}\right) = -8.138 + \frac{Ae}{4\pi\in_0 R_e} \text{ in eV}$$

$$= -8.138 + \frac{1.75 \times 1.6 \times 10^{-19} \times 9 \times 10^9}{2.82 \times 10^{-10}}$$

$$= -8.138 + 8.936$$

$$= 0.798$$

or
$$B = 0.798 \times \exp\left(\frac{R_e}{\rho}\right)$$

$$= 0.798 \times \exp\left(\frac{2.82}{0.25}\right)$$

$$= 63.22 \times 10^3 \text{ eV}$$

Example 3.20 How many atoms are there in *sc*, *bcc* and *fcc* unit cells? Calculate the packing efficiency or (packing factor) in each case.

Solution: The number of atoms per unit cell is given by

$$n = \frac{N_c}{8} + \frac{N_f}{2} + N_b \tag{1}$$

where N_c = No. of corner atoms

N_f = No. of face centered atoms

N_b = No. of body centered atoms

With the help of Eq. 1 and the knowledge of corner, face centered and body centered atoms, the number of atoms in cubic unit cells can be obtained easily. We can obtain this for

$$sc, n = 1$$

$$bcc, n = 2$$

$$fcc, n = 4$$

Now, the relationship between a (unit cell parameter) and R (radius of the atom) for three cubic cases are (Fig. 3.3):

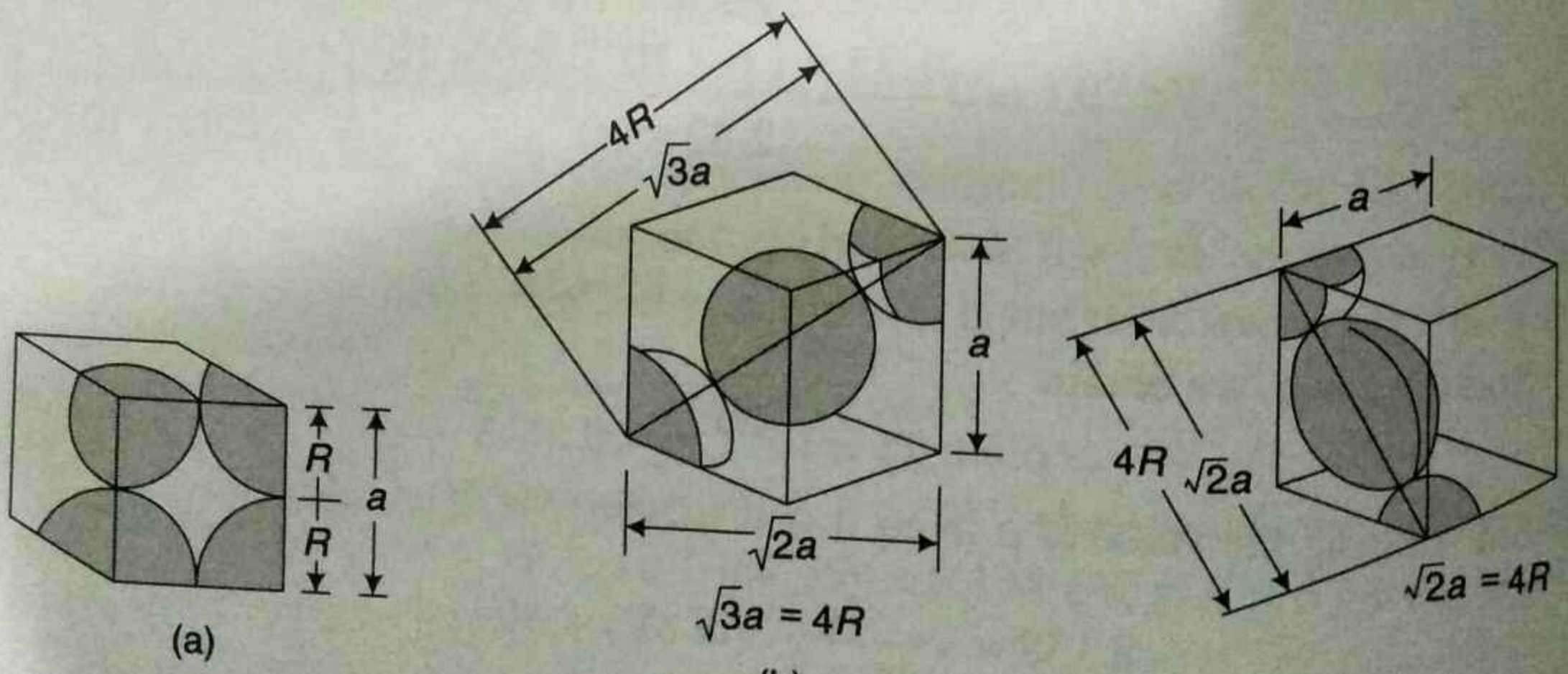


Fig. 3.3 Sectional view of conventional cubic unit cells showing relationship between the lattice constant a and the atomic radius R in: (a) a simple cubic unit cell, (b) a body centred unit cell, (c) a face centred unit cell

For

$$sc : a = 2R \quad \text{so that} \quad V_{sc} = (a)^3 = (2R)^3 = 8R^3$$

$$bcc : \sqrt{3}a = 4R \quad \text{so that} \quad V_{bcc} = (a)^3 = \left(\frac{4R}{\sqrt{3}}\right)^3 = \frac{64R^3}{3\sqrt{3}}$$

$$fcc : \sqrt{2}a = 4R \quad \text{so that} \quad V_{fcc} = (a)^3 = (2\sqrt{2}R)^3 = 16\sqrt{2}R^3$$

Their packing factors are determined by using the formula

$$P.F = \frac{\text{Vol. of the atoms (in the unit cell)}}{\text{Vol. of the unit cell}} \quad (2)$$

Therefore, $(P.F)_{sc} = \dfrac{1 \times (4\pi R^3)/3}{8R^3} = \dfrac{\pi}{6} = 52\%$

$$(P.F)_{bcc} = \frac{2 \times (4\pi R^3)/3}{64R^3/3\sqrt{3}} = \frac{\sqrt{3}}{8}\pi = 68\%$$

$$(P.F)_{fcc} = \frac{4(4\pi R^3)/3}{16\sqrt{2}R^3} = \frac{\pi}{3\sqrt{2}} = 74\%$$

Example 3.21 Show that for an ideal *hcp* structure, where the atomic spheres touch each other, the axial ratio *c*/*a* is given by

$$c/a = (8/3)^{1/2} = 1.633$$

Solution: Let us consider a conventional *hcp* unit cell (Fig. 3.4a). Replace each point by a hard sphere of radius R such that they touch each other as in Fig. 3.5a. In an ideal *hcp* structure $a = 2R$ and c is limited by the fact that the distance between the two basis atoms-one at the origin 000 and the other at $\frac{2}{3}\frac{1}{3}\frac{1}{2}$ – must be equal to $2R$. This distance is marked as D in Fig. 3.5b. So that,

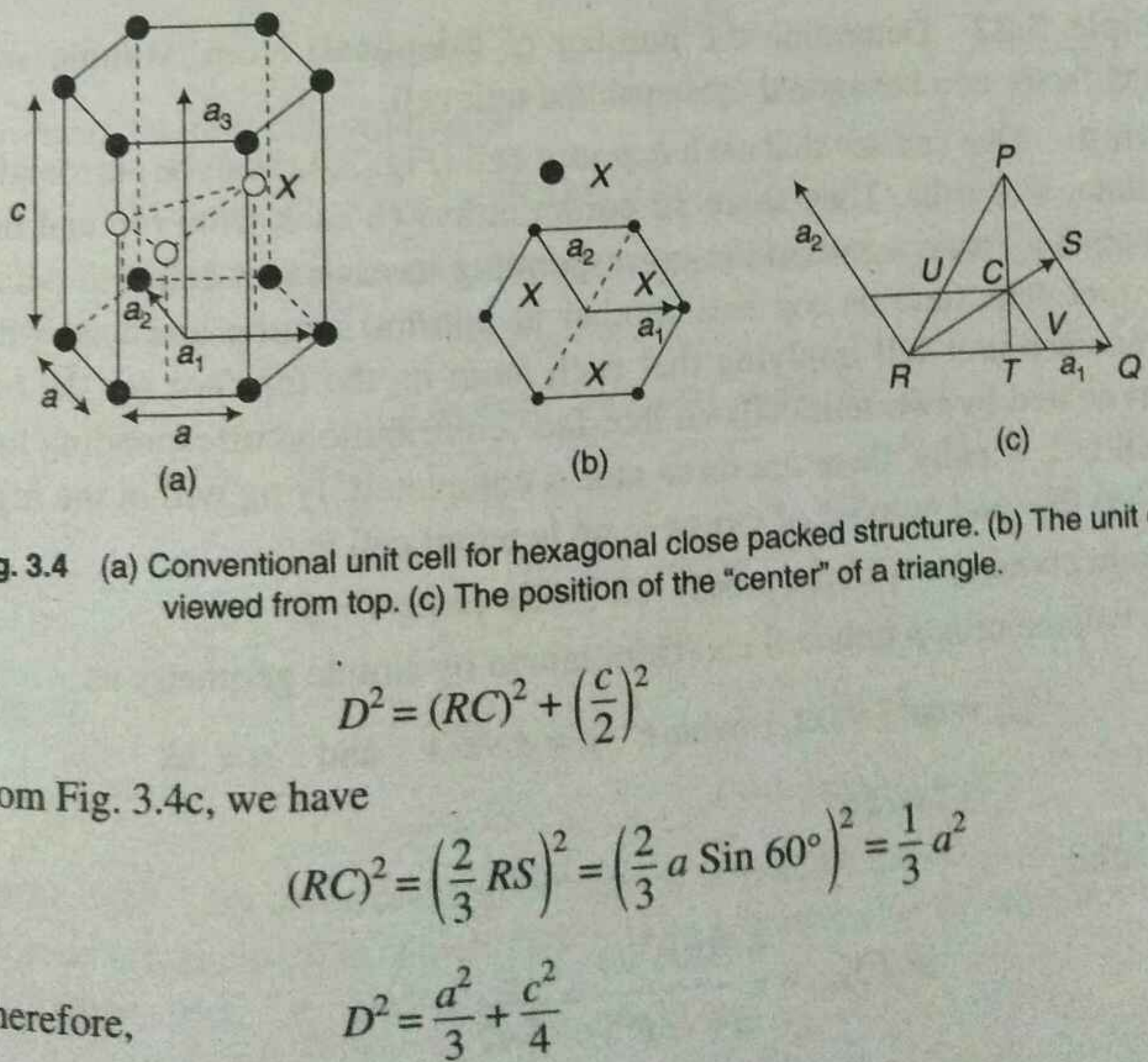


Fig. 3.4 (a) Conventional unit cell for hexagonal close packed structure. (b) The unit cell viewed from top. (c) The position of the "center" of a triangle.

$$D^2 = (RC)^2 + \left(\frac{c}{2}\right)^2$$

From Fig. 3.4c, we have

$$(RC)^2 = \left(\frac{2}{3}RS\right)^2 = \left(\frac{2}{3}a\,\text{Sin}\,60^\circ\right)^2 = \frac{1}{3}a^2$$

Therefore, $$D^2 = \frac{a^2}{3} + \frac{c^2}{4}$$

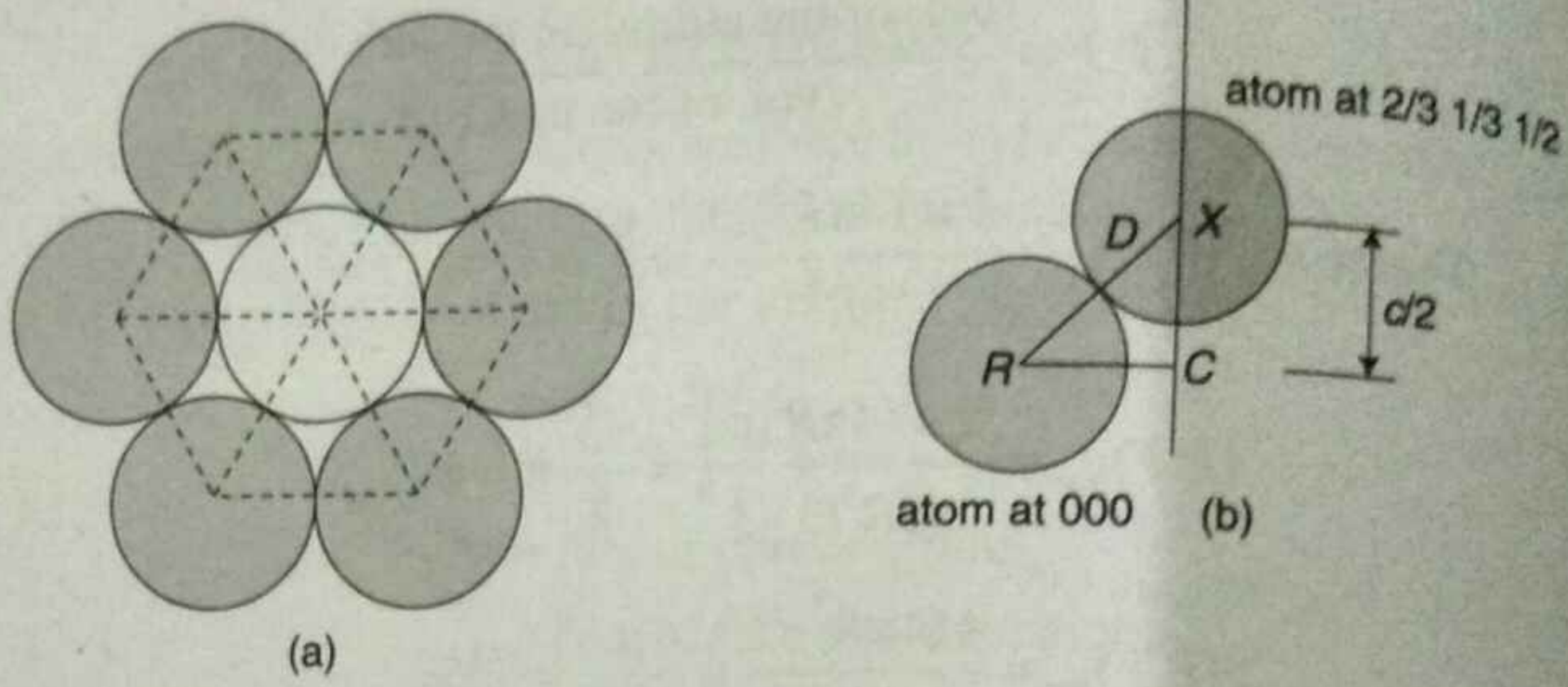


Fig. 3.5 Packing of equal spheres in hexagonal close packed lattice

But $D = 2R$ and $a = 2R$, so that $D = a$. Therefore,

$$a^2 = \frac{a^2}{3} + \frac{c^2}{4}$$

Further simplifying, we get

$$c^2 = \frac{8}{3}a^2$$

or

$$\frac{c}{a} = \left(\frac{8}{3}\right)^{1/2} = 1.633$$

Example 3.22 Determine the number of (identical) atom, volume and the packing factor of a hexagonal close packed unit cell.

Solution: One can see that each *hcp* unit cell (Fig. 3.4a) can be surrounded by six similar unit cells. They share 12 corner atoms (6 each from top and bottom layer) so that corner contribution corresponding to each unit cell is 2. Similarly 2 *hcp* unit cells (one on top and another at bottom) can be arranged with the reference *hcp* unit cell implying that each atom on the top face (or the bottom face) is shared by two unit cells so that face contribution corresponding to each unit cell is 1. Finally, there are three atoms completely lying within the *hcp* unit cell. Thus the total number of atoms in an *hcp* unit cell is

2 (from corners) + 1 (from sides) + 3 (body center) = 6

The volume of *hcp* unit cell can be obtained by simple geometry as

$$V_{hcp} = ca^2 3\sqrt{3}/2, \quad \text{where} \quad c = a\sqrt{8/3} \quad \text{and} \quad a = 2R$$

$$= 24\sqrt{2}R^3$$

Therefore,

$$(P.F)_{hcp} = \frac{6(4\pi R^3)/3}{24\sqrt{2}R^3} = \frac{\pi}{3\sqrt{2}} = 74\%$$

Example 3.23 Calculate the packing factor of a sodium chloride structure. The ionic radii of Na^+ and Cl^- are 0.98 Å and 1.81 Å, respectively.

Solution: Given: The ionic radius of $Na^+ = 0.98$ Å, $Cl^- = 1.81$ Å, $(PF)_{NaCl} = ?$ The structure of NaCl is shown in Fig. 3.6. The Na^+ and Cl^- ions touch each other, so that

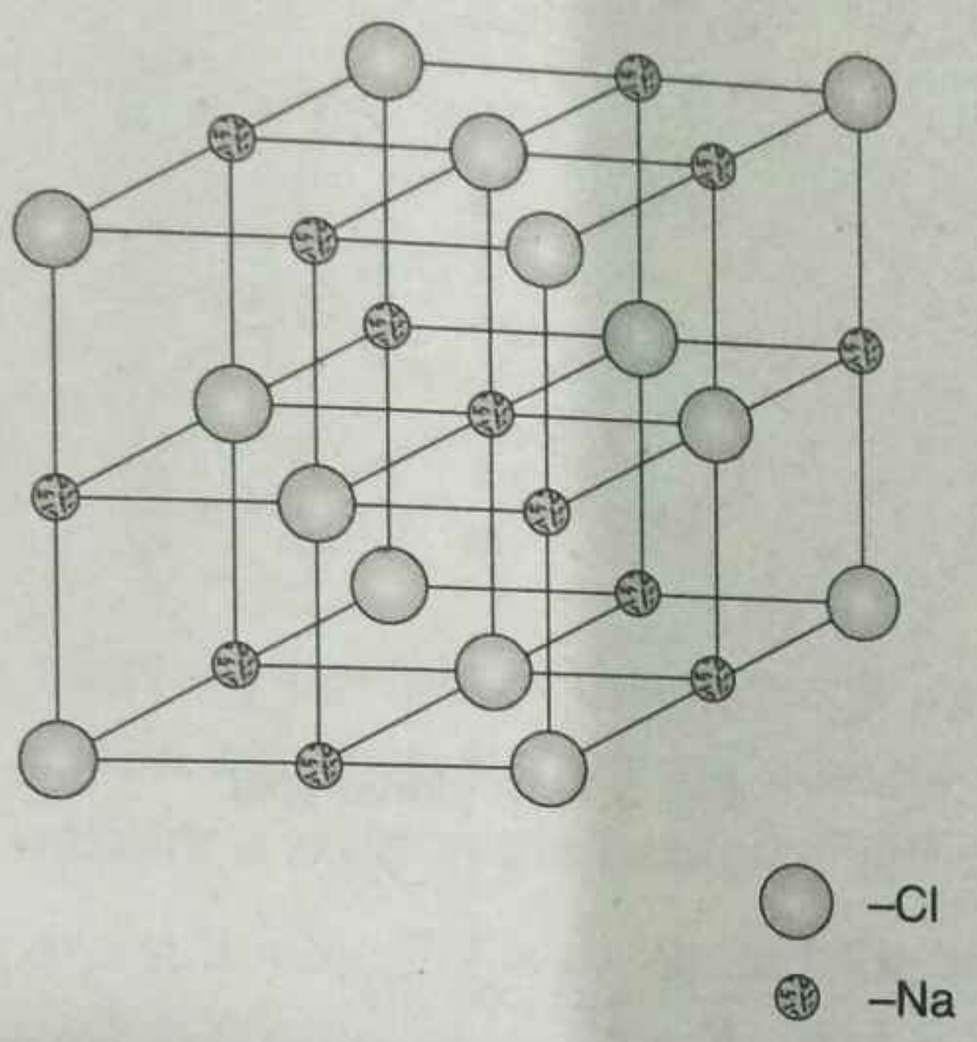


Fig. 3.6 Sodium chloride crystal structure

$$a = 2 \text{ (radius of } Na^+ + \text{radius of } Cl^-)$$

$$= 2 (0.98 + 1.81)$$

$$= 5.58 \text{ Å}$$

Therefore, the unit cell volume is

$$V = a^3 = (5.58)^3 \text{ Å}^3$$

Further in Fig. 3.6, we observe that there are 4 NaCl molecules in a unit cell. Therefore, according to the definition

$$(P.F)_{NaCl} = \frac{4\left(4\pi R^3_{Na^+}\right)/3 + 4\left(4\pi R^3_{Cl^-}\right)/3}{a^3}$$

$$= \frac{16}{3}\pi\left[\frac{(0.98)^3 + (1.81)^3}{(5.58)^3}\right]$$

$$= 0.66.3$$

$$= 66.3\%$$

Example 3.24 By using plane geometry calculate the cation – cation ratio for a triangular arrangement in which cation is in contact with the anions but does not push them apart.

Solution: Let us consider the critical condition of a triangular arrangement of anions and a cation at the site of the triangular void touching the anions, where anions also touch each other as shown in Fig. 3.7. Let r be the radius of the central cation and R be the radius of the anions. From simple geometrical construction in Fig. 3.7, we have

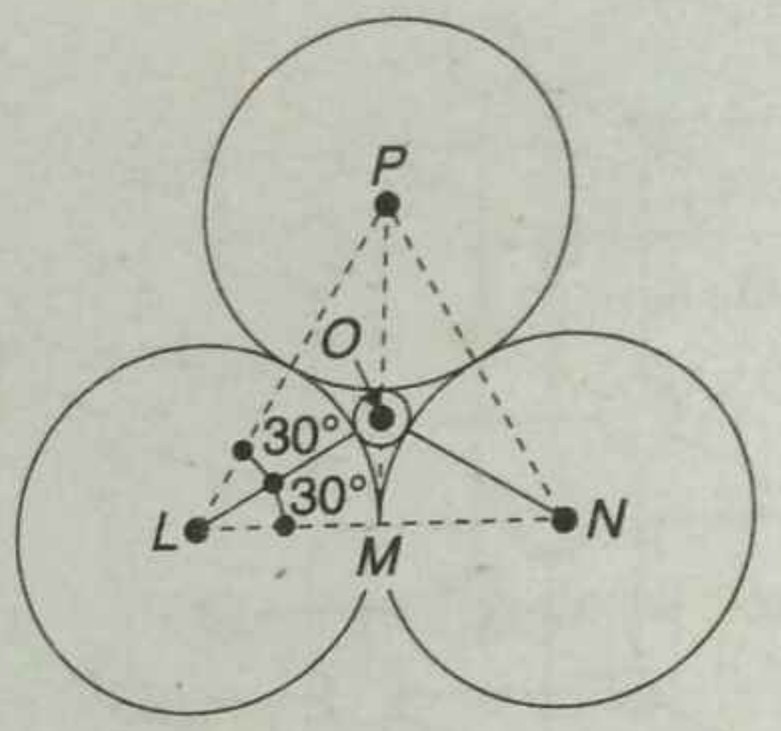


Fig. 3.7 A planar void

$$\frac{LM}{LO} = \frac{R}{R+r} = \cos 30°$$

or
$$r = \frac{R}{\cos 30°} - R = \frac{2}{\sqrt{3}} R - R = 1.155R - R = 0.155\,R$$

or
$$\frac{r}{R} = 0.155$$

Example 3.25 Show that critical radius ratio for a tetrahedral coordination is 0.225.

Solution: Let us consider a tetrahedral void surrounded by four spheres of radius R (Fig. 3.8a). The centers of the spheres lie at the corners of a regular tetrahedron of side $a = 2R$ and height h (Fig. 3.8b). For a regular tetrahedron of side a, $a \sin 60°$ is the median of any four bounding faces. In a triangle BPQ (shown separately in Fig. 3.8c), P is the mid point of one side of the base and Q is the centroid, then

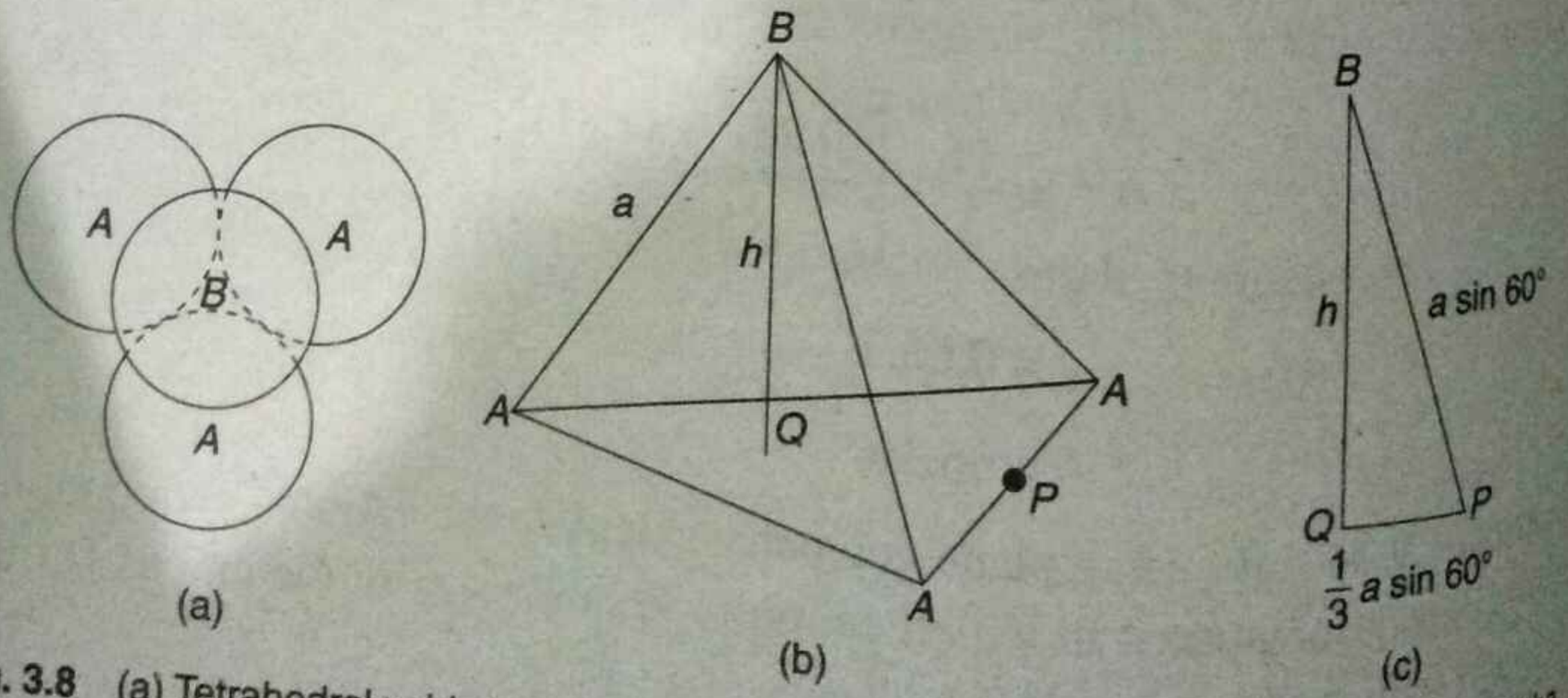


Fig. 3.8 (a) Tetrahedral voids in a close packing (b) Tetrahedron formed by the centres of the spheres (c) Section BPQ of Fig. 3.10 (b)

$$BP = a \sin 60°, PQ = \frac{1}{3} a \sin 60°$$

and $$(BP)^2 = (BQ)^2 + (QP)^2$$

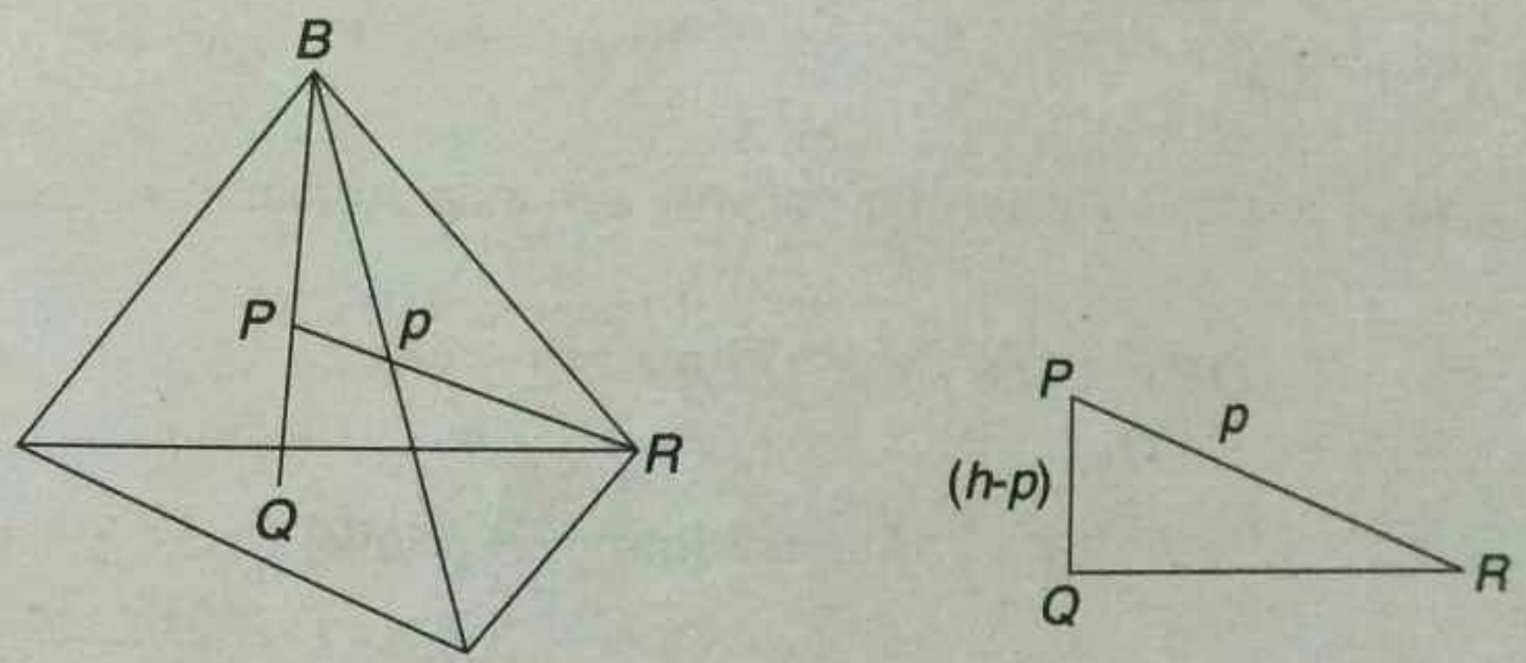
or $$a^2 \sin^2 60° = h^2 + \frac{a^2}{9} \sin^2 60°$$

or $$h^2 = a^2 \sin^2 60° \left(1 - \frac{1}{9}\right)$$

or $$\frac{h^2}{a^2} = \frac{3}{4} \times \frac{8}{9}$$

or $$\frac{h}{a} = \frac{\sqrt{2}}{\sqrt{3}} \qquad (1)$$

Now, let r be the radius of the sphere that just fits into the tetrahedral void whose center is at P and is equidistant from all corners (Fig. 3.9a). The bond length is $p = r + R$. Consider a right angle triangle PQR separately as shown in Fig. 3.9b, where the perpendicular $PQ = h - p$ and the base $QR = \frac{2}{3} a \sin 60°$. From the triangle PQR, we can write



(a) (b)

Fig. 3.9 (a) A tetrahedron (b) Section *PQR* of Fig. 3.9 (a)

$$(PR)^2 = (PQ)^2 + (QR)^2$$

or $$p^2 = (h - p)^2 + \frac{h^2}{2} \qquad (2)$$

so that, $$p = \frac{3}{4} h$$

Substituting the value of p and h in terms of r and R in eq. 2, we have

$$r + R = \frac{3}{4} \cdot \frac{\sqrt{2}}{\sqrt{3}} \cdot 2R = \frac{\sqrt{3}}{\sqrt{2}} R$$

or $$r = \frac{\sqrt{3} - \sqrt{2}}{\sqrt{2}} R = 0.225\, R$$

Therefore, $\frac{r}{R} = 0.225$

Example 3.26 Show that the critical radius ratio for an octahedral coordination is 0.414.

Solution: Let us consider an octahedral void surrounded by six spheres (three in each upper and lower layer) of radius R, the centers of the spheres lie at the corners of a regular octahedron of side $a = 2R$. The projection of the centers of the six spheres is shown in Fig. 3.10a. The point O represents the center of the sphere fitted in the octahedral void. The bond length $OR = p = r + R$. Now from the right angled triangle $OO'R$ shown separately in Fig. 3.10b (where O' lies in the plane of upper layer), we have

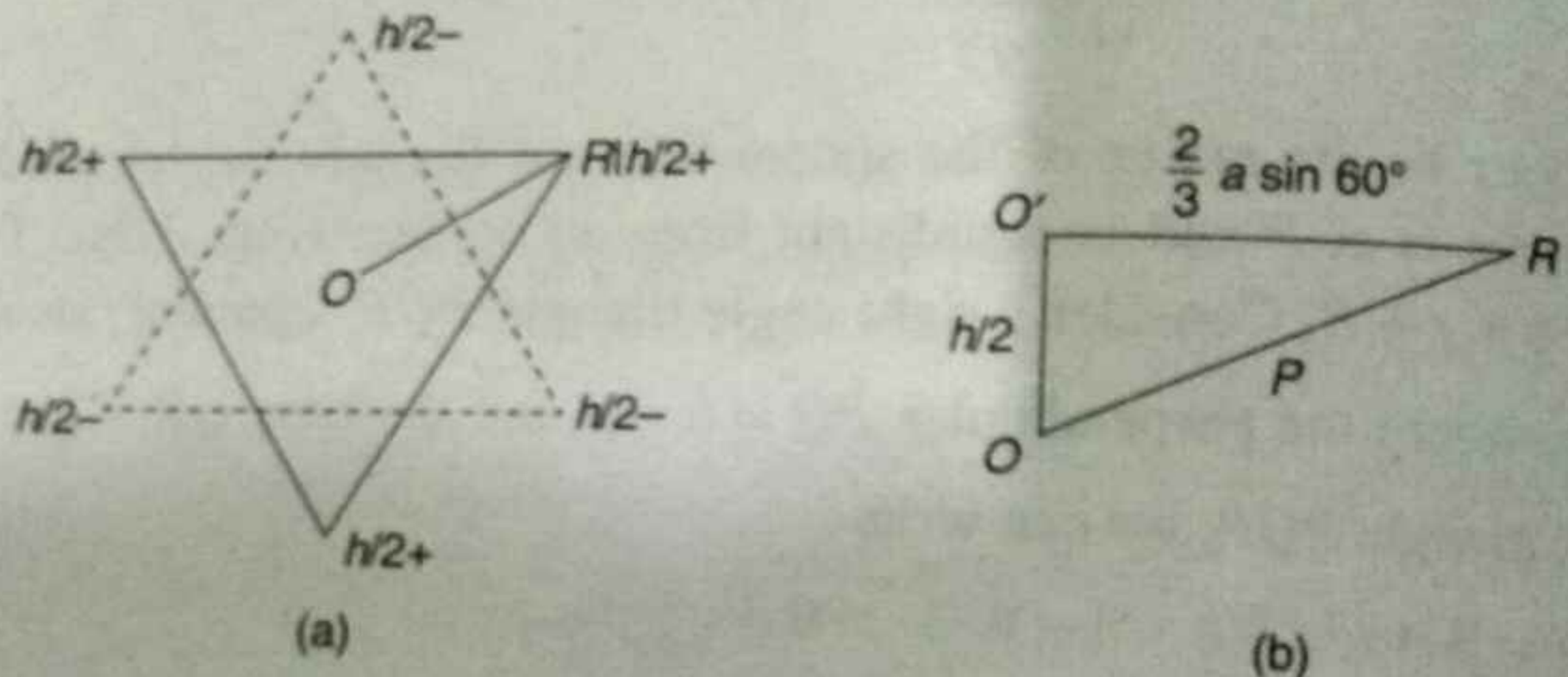


Fig. 3.10 Projection of centres of spheres with their position coordinates

$$(OR)^2 = (OO')^2 + (O'R)^2$$

or $$p^2 = \left(\frac{h}{2}\right)^2 + \frac{h^2}{2} \left(\text{where } \frac{\sqrt{2}}{\sqrt{3}} a = h\right)$$

or $$p = \frac{\sqrt{3}}{2} h \qquad (1)$$

Substituting the value of p and h in terms of r and R in eq. 1, we have

$$r + R = \sqrt{2}R$$

or $$r = (\sqrt{2} - 1)R = 0.414R$$

Therefore, $\frac{r}{R} = 0.414$

Example 3.27 Calculate the void space in a close packing of n spheres of radius 1.000, n spheres of radius 0.414 and $2n$ spheres of radius 0.225.

Solution: Let us consider the case of cubic close packing, i.e. equivalently the packing in the face centered cubic unit along [111] direction. In this case the side of the unit cell and the radius of the sphere is related (Fig. 3.3c) as

$$\sqrt{2}\,a = 4R \quad \text{or} \quad a = 2\sqrt{2}R$$

Therefore, the volume of the unit cell is

$$V = a^3 = 16\sqrt{2}R^3 = 16\sqrt{2} \text{ (for } R = 1)$$

Further, for *fcc* the number of atoms in the unit cell, $n = 4$. The volume occupied is

$$V = 4 \times \frac{4}{3}\pi\left[(1.000)^3 + (0.414)^3 + 2 \times (0.225)^3\right]$$

$$= 18.319$$

The void space is obtained as

Void space = Total volume – Occupied volume

$$= 16\sqrt{2} - 18.319$$

$$= 4.308$$

$$= 19\%$$

Example 3.28 Find the diameter of the largest atom that would fit into the void in *fcc* nickel without distortion.

Solution: For *Ni*, the lattice parameter, $a = 3.52$ Å.

Also for an *fcc* lattice, we know that $\sqrt{2}a = 4R$, so that

$$R = \frac{\sqrt{2}a}{4} = \frac{\sqrt{2} \times 3.52}{4} = 1.2445 \text{ Å}$$

Since *fcc* structure for a monoatomic solid is close packed and the largest void in a close packing is an octahedral void (equivalent to the largest atom in question). Therefore,

$$R_{oct} = 0.414\,R = 0.414 \times 1.2445 = 0.515 \text{ Å}$$

Thus the diameter of the largest atom D_{LA} will be equal to the diameter of the octahedral void in the structure. Therefore,

$$D_{LA} = D_{oct} = 2R_{oct} = 2 \times 0.515 = 1.03 \text{ Å}$$

Example 3.29 Calculate the ratio of the volumes of a tetrahedron and an octahedron having the same edge length.

Solution: A tetrahedron and an octahedron are shown in Fig. 3.11 and Fig. 3.12, respectively. They contain 4 atoms and 6 atoms, respectively, one at each corner. In a close packing, they have the same edge length, say a. Their volumes can be determined by using the standard formula, i.e. the volume of a tetrahedron is

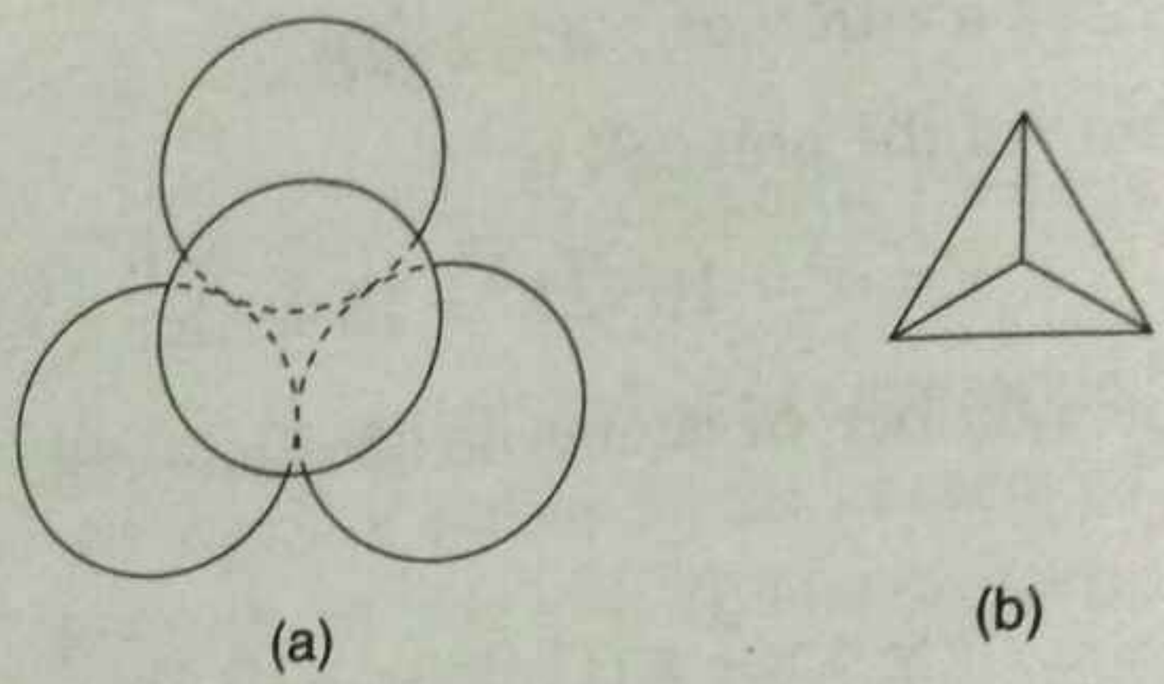


Fig. 3.11 (a) A tetrahedral void (b) Projection of centre of spheres

$$V_t = \frac{1}{3} Ah \tag{1}$$

where A is the base area and h is the height of the next close packed layer. Substituting the values of A and h in terms of a in eq. 1, we have

$$V_t = \frac{1}{3} Ah = \frac{1}{3} \times \frac{\sqrt{3}}{4} a^2 \times \frac{\sqrt{2}}{\sqrt{3}} a$$

$$= \frac{a^3}{6\sqrt{2}}$$

Similarly, the volume of an octahedron is,

$$V_o = \frac{2}{3} Ah = \frac{2}{3} a^2 \times \frac{\sqrt{2}}{\sqrt{3}} a$$

$$= \frac{2\sqrt{2}}{3\sqrt{3}} a^3$$

Therefore, the ratio of their volumes is,

$$\frac{V_t}{V_o} = \frac{a^3}{6\sqrt{2}} \times \frac{3 \times \sqrt{3}}{2\sqrt{2} a^3} = \frac{\sqrt{3}}{8} = 0.216$$

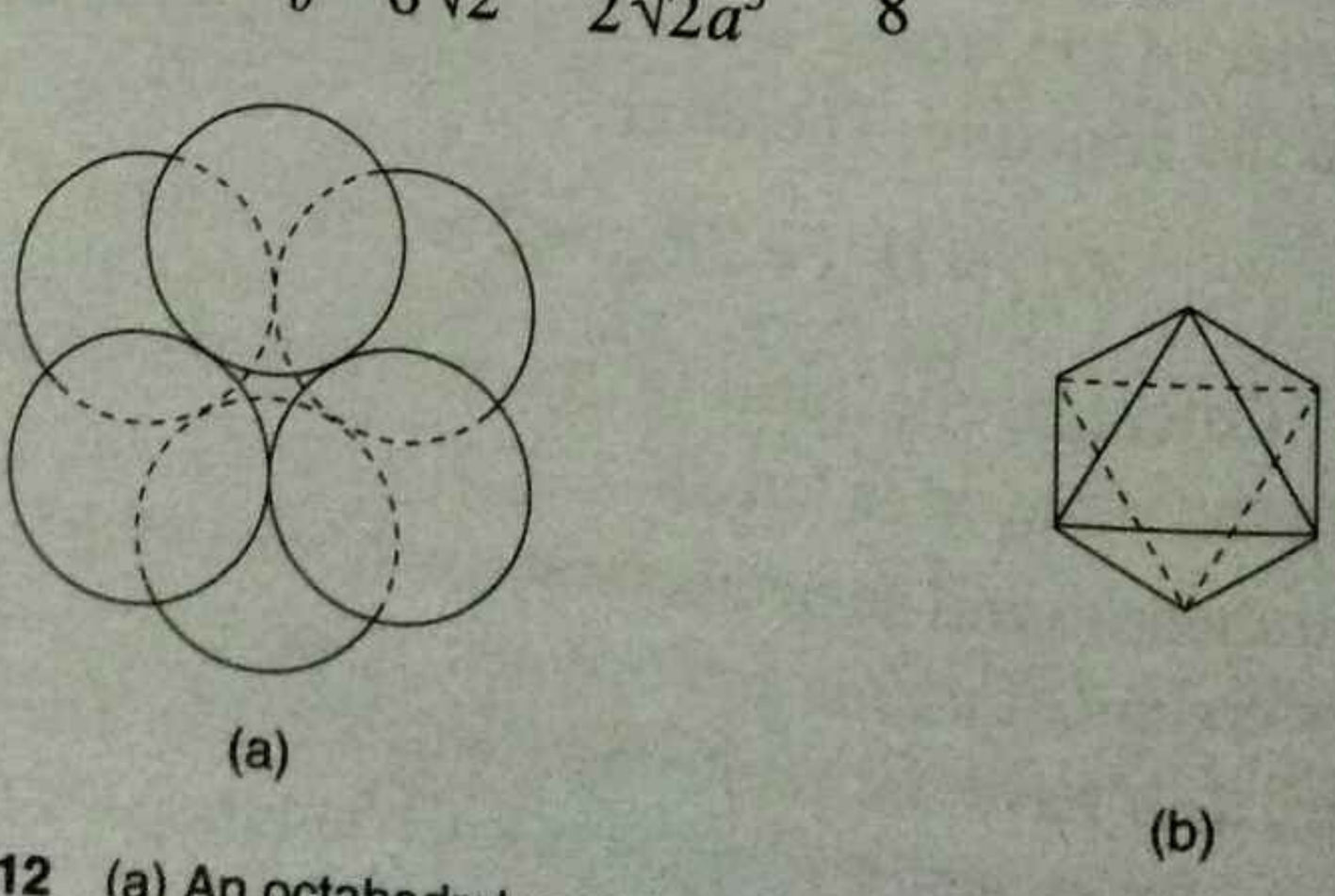


Fig. 3.12 (a) An octahedral void (b) Projection of centre of spheres

Example 3.30 Determine the nearest neighbour distance in *bcc* and *fcc* structures when the atomic radius is given as 10 Å.

Solution: Given: Radius of the atom, $R = 10$ Å, nearest neighbour distance, say $d_{bcc} = ?, d_{fcc} = ?$

We know that the nearest neighbour distance in a *bcc* structure is half of the body diagonal, i.e. $d_{bcc} = \frac{\sqrt{3}a}{2}$, where a is the side of the cube. But the limiting condition (Fig. 3.3*b*) in a *bcc* structure is

$$\sqrt{3}a = 4R$$

or
$$\frac{\sqrt{3}a}{2} = 2R = 2 \times 10 = 20 \text{ Å}$$

Similarly, the nearest neighbour distance in an *fcc* structure is half of the face diagonal, i.e.

$$d_{fcc} = \frac{\sqrt{2}a}{2} = \frac{a}{\sqrt{2}},$$

where a is the side of the cube.

But the limiting condition (Fig. 3.3*c*) in an *fcc* structure is

$$\sqrt{2}a = 4R$$

or
$$\frac{\sqrt{2}a}{2} = 2R = 2 \times 10 = 20 \text{ Å}$$

Review Questions

3.1 The potential energy of diatomic molecule in terms of the interatomic separation R is given by

$$U(R) = -\frac{A}{R^2} + \frac{B}{R^{10}}$$

A stable molecule is formed with the release of 8.0 eV of energy when the interatomic distance is 2.8 Å. Calculate A and B. Determine the force needed to dissociate this molecule into atoms and the interatomic distance at which the dissociation occurs.
Ans. 1.254×10^{-37} Jm^2, 9.48×10^{-115} Jm^{10}, $5.08 \times 10^{-19} N$, 3.3×10^{-10} m.

3.2 The lattice energy of KCl crystal containing N molecules of KCl is given by

$$U(R) = -N\left(\frac{Ae^2}{R} - \frac{B}{R^n}\right)$$

Determine the repulsive exponent n using the following data:
Nearest neighbour equilibrium distance, $R_e = 3.147$ Å
Compressibility of KCl, $K = 5.747 \times 10^{-11}$ m^2/N
Madelung constant, $A = 1.748$ *Ans.* 8.63

3.3 The potential energy of two atoms in the field of each other is given by

$$U(R) = -\frac{A}{R} + \frac{B}{R^9}$$

where A and B are constants. Show that (a) the atoms form a stable compound when $R = R_e\,(9B/A)^{1/8}$ (b) for stable configuration, the energy of attraction n is nine times the energy of repulsion, and (c) the potential energy of the system under stable configuration is $(8A/9R_e)$.

3.4 The potential energy of a diatomic molecule in terms of the interatomic separation R is given by

$$U(R) = -\frac{A}{R^2} + \frac{B}{R^{10}}$$

where $A = 1.44 \times 10^{-39}$ Jm^2 and $B = 2.19 \times 10^{-115}$ Jm^{10}. Calculate the equilibrium spacing R_e and the dissociation energy.

Ans. 4.08×10^{-10} m, 4.33×10^{-2} eV

3.5 Determine the potential energy of NaCl at equilibrium, if the separation between sodium and chlorine atoms is 2.81 Å, $A = 1.7476$ and $n = 9$.

Ans. – 7.96 eV

3.6 In an MX molecule, the ionization potential of M atom is 5 eV and the electron affinity of X atom is 4 eV. Determine the energy required to transfer an electron from M to X when they are at a distance of 5 Å.

Ans. – 1.88 eV

3.7 Calculate the potential energy of the system of Na^+ and Cl^- ions when they are 2 Å apart. *Ans.* – 7.2 eV

3.8 Show that the critical radius ratio for a cubic coordination is 0.732.

3.9 Determine the packing efficiency of equal spheres located at the points of simple hexagonal and hexagonal close packed lattices.

Ans. 68% and 74%

3.10 Determine the packing efficiency in the diamond structure. *Ans.* 34%

3.11 Find the diameter of the largest sphere that will fit into the void produced by the *bcc* packing of atoms of radius R. The void is located at (0 1/2 1/4) and other equivalent positions. *Ans.* 0.29R

3.12 Calculate the ratio of cation-anion distance to anion-anion distance in an anion coordination tetrahedron. *Ans.* 0.612

3.13 Calculate the attractive force between a pair of Mg^{2+} and O^{2-} ions that just touch each other. Assume that the ionic radius of the Mg^{2+} ion to be 0.65 Å and that of O^{2-} ion to be 1.40 Å.
Ans. $2.19 \times 10^{-8} N$

3.14 Calculate the limit of ionic radius ratio for the stability of NaCl structure, and compare this with the actual radius ratio for NaBr and NaI having NaCl structure.
Ans. 0.414 – 1/0.414

3.15 What is the coordination number of Manganese in *MnO* structure if $r_{Mn} = 0.80$ Å and $r_O = 1.40$ Å.
Ans. 6 : 6

Multiple choice Questions

3.1 The potential energy of a diatomic molecule in terms of interatomic distance R is given by

$$U(R) = -\frac{A}{R^m} + \frac{B}{R^n}$$

where A, B, m and n are constants characteristics for the MX – molecules. Attractive and repulsive exponents are related through:

(a) $n << m$ (b) $n < m$ (c) $n > m$ (d) $n >> m$

3.2 The potential energy of a diatomic molecule in terms of interatomic distance R is given by

$$U(R) = -\frac{A}{R^m} + \frac{B}{R^n}$$

where A, B, m and n are constant characteristics for the MX – molecules. The equilibrium separation R_e is obtained as:

(a) $\left(\frac{nA}{mB}\right)^{\frac{1}{n-m}}$ (b) $\left(\frac{nA}{mB}\right)^{\frac{1}{m-n}}$ (c) $\left(\frac{nB}{mA}\right)^{\frac{1}{m-n}}$ (d) $\left(\frac{nB}{mA}\right)^{\frac{1}{n-m}}$

3.3 The potential energy of a diatomic molecule in terms of interatomic separation R is given by

$$U(R) = -\frac{\alpha}{R^4} + \frac{\beta}{R^{12}}$$

The equilibrium separation is obtained as:

(a) $(3\beta/\alpha)^{1/8}$ (b) $(3\beta/\alpha)^{1/6}$ (c) $(3\beta/\alpha)^{1/4}$ (d) $(3\beta/\alpha)^{1/2}$

3.4 The potential energy of a diatomic molecule in terms of interatomic distance R is given by

$$U(R) = -\frac{\alpha}{R^4} + \frac{\beta}{R^{14}}$$

The equilibrium energy when the molecule is stable is:

(a) $\left(\frac{4\alpha^3}{27\beta}\right)^{1/2}$ (b) $-\left(\frac{4\alpha^3}{27\beta}\right)^{1/2}$

(c) $\left(\frac{4\alpha^3}{27\beta}\right)^{1/4}$ (d) $-\left(\frac{4\alpha^3}{27\beta}\right)^{1/4}$

3.5 The potential energy of a system of two atoms is given by

$$U = -\frac{A}{R^6} + \frac{B}{R^{12}}$$

If the atoms form a stable bond with bond length 3 Å and the bond energy 1.8 eV, the value of the constant A is:

(a) 1.19×10^{-76} Jm^6 (b) 2.19×10^{-76} Jm^6

(c) 3.19×10^{-76} Jm^6 (d) 4.19×10^{-76} Jm^6

3.6 The potential energy of a system of two atoms is given by

$$U = -\frac{A}{R^6} + \frac{B}{R^{12}}$$

If the atoms form a stable bond with bond length 3 Å and the bond energy 1.8 eV, the critical separation R_c is obtained as:

(a) 1.33 Å (b) 2.33 Å (c) 3.33 Å (d) 4.33 Å

3.7 If the equilibrium separation between cesium and chlorine atoms is 3.56 Å, $A = 1.76$ and $n = 11.5$, the potential energy of CsCl at equilibrium is:

(a) – 2.5 eV (b) – 4.5 eV (c) – 6.5 eV (d) – 8.5 eV

3.8 A pair of Li^+ and Cl^- ion with their radii 0.60 Å and 1.81 Å touch each other, the attractive force between them is:

(a) $1.96 \times 10^{-9} N$ (b) $2.96 \times 10^{-9} N$

(c) $3.96 \times 10^{-9} N$ (d) $4.96 \times 10^{-9} N$

3.9 Show that the Madelung constant A for an infinite linear chain of ions of alternating charge at an equilibrium separation R_e is:

(a) 0.3863 (b) 1.3863 (c) 2.3863 (d) 3.3863

3.10 Show that the potential energy of two particles in stable configuration (at equilibrium) with $m = 2$ and $n = 10$ is equal to:

(a) $-\frac{1}{5}\left(\frac{A}{R_e^2}\right)$ (b) $-\frac{2}{5}\left(\frac{A}{R_e^2}\right)$ (c) $-\frac{3}{5}\left(\frac{A}{R_e^2}\right)$ (d) $-\frac{4}{5}\left(\frac{A}{R_e^2}\right)$

3.11 Show that the Madelung constant for an infinite array of two dimensional ionic charge distribution (i.e. two dimensional NaCl crystal) with equilibrium ion separation as R_e is:

(a) 1.6135 (b) 2.6135 (c) 3.6135 (d) 4.6135

3.12 The lattice parameter of NaCl is 5.63 Å, n is 9 and the Madelung constant A is 1.75. Show that the binding energy per molecule is:

(a) 4.95 eV (b) 5.95 eV (c) 6.95 eV (d) 7.95 eV

3.13 Assume a repulsive potential of the form B/R^9 acts between the neighbouring ions of NaCl. If the nearest neigbour distance is 2.81 Å and the Madelung constant is 1.7476, the compressibility of NaCl is:

(a) 2.48×10^{-11} m^2N (b) 3.48×10^{-11} m^2N

(c) 4.48×10^{-11} m^2N (d) 5.58×10^{-11} m^2N

3.14 If an atom A has an ionization energy 5 eV, another atom B has an electron affinity 4 eV and they are 5 Å apart. Show that the energy required to transfer an electron from A to B is:

(a) – 1.88 eV (b) – 2.88 eV (c) – 3.88 eV (d) – 4.88 eV

3.15 The ionization potential of K (potassium) is 4.1 eV and the electron affinity of Cl (chlorine) is 3.6 eV. If the total energy of K^+ and Cl^- ion pair is zero, show that the separation between them is:

(a) 7.8 Å (b) 14.8 Å (c) 21.8 Å (d) 28.8 Å

3.16 If the equilibrium bond distance of NaCl is 2.81 Å, the Madelung constant is 1.748 and the repulsion exponent is 0.32 Å, show that the cohesive energy of NaCl is:

(a) – 6.94 eV (b) – 7.94 eV (c) – 8.94 eV (d) – 9.94 eV

3.17 The number atoms in a *bcc* unit cell is:

(a) 1 (b) 2 (c) 4 (d) 8

3.18 The number atoms in a *fcc* unit cell is:

(a) 1 (b) 2 (c) 4 (d) 8

3.19 The number of atoms in a diamond cubic (*DC*) unit cell is:

(a) 1 (b) 2 (c) 4 (d) 8

3.20 The number of atoms in a simple hexagonal (*SH*) unit cell is:

(a) 2 (b) 3 (c) 4 (d) 6

3.21 The number of atoms in a *hcp* unit cell is:

(a) 2 (b) 3 (c) 4 (d) 6

3.22 The packing efficiency of a simple cubic (*SC*) structure is:

(a) 34% (b) 52% (c) 60% (d) 68%

3.23 The packing efficiency of a *bcc* structure is:

(a) 34% (b) 52% (c) 60% (d) 68%

3.24 The packing efficiency of a diamond cubic (*DC*) structure is:

(a) 34% (b) 52% (c) 60% (d) 68%

3.25 The packing efficiency of an *fcc* structure is:

(a) 34% (b) 52% (c) 68% (d) 74%

3.26 The packing efficiency of a simple hexagonal (*SH*) structure is:

(a) 52% (b) 60% (c) 68% (d) 74%

3.27 The packing efficiency of an *hcp* structure is:

(a) 52% (b) 60% (c) 68% (d) 74%

3.28 The axial ratio (*c*/*a*) of an ideal hexagonal close packing is:

(a) 1.633 (b) 2.633 (c) 3.633 (d) 4.633

3.29 The size of a tetrahedral void in a close packing of equal spheres of radius *R* is:

(a) 0.155 (b) 0.225 (c) 0.414 (d) 0.732

3.30 The size of an octahedral void in a close packing of equal spheres of radius *R* is:

(a) 0.155 *R* (b) 0.225 *R* (c) 0.414 *R* (d) 0.732 *R*

Answers

1. (c)	2. (d)	3. (a)	4. (b)	5. (d)	6. (c)	7. (c)
8. (c)	9. (b)	10. (d)	11. (a)	12. (d)	13. (b)	14. (a)
15. (d)	16. (b)	17. (b)	18. (c)	19. (d)	20. (b)	21. (d)
22. (b)	23. (d)	24. (a)	25. (d)	26. (b)	27. (d)	28. (a)
29. (b)	30. (c)					

CHAPTER 4

Crystal Imperfections and Atomic Diffusion

IMPORTANT FORMULAE

4.1 (a) The Configurational entropy for arranging n identical vacancies and $(N\text{-}n)$ identical atoms on N sites is given by

$$S_{cf} = kln\left[\frac{N!}{(N\text{-}n)!n!}\right]$$

(b) Vacancy (Fig. 4.1) concentration in a monoatomic solid at a certain temperature T is given by

$$n = \text{Nexp}\left(-\frac{E_v}{kT}\right) = \text{Nexp}\left(-\frac{\Delta Hf}{RT}\right)$$

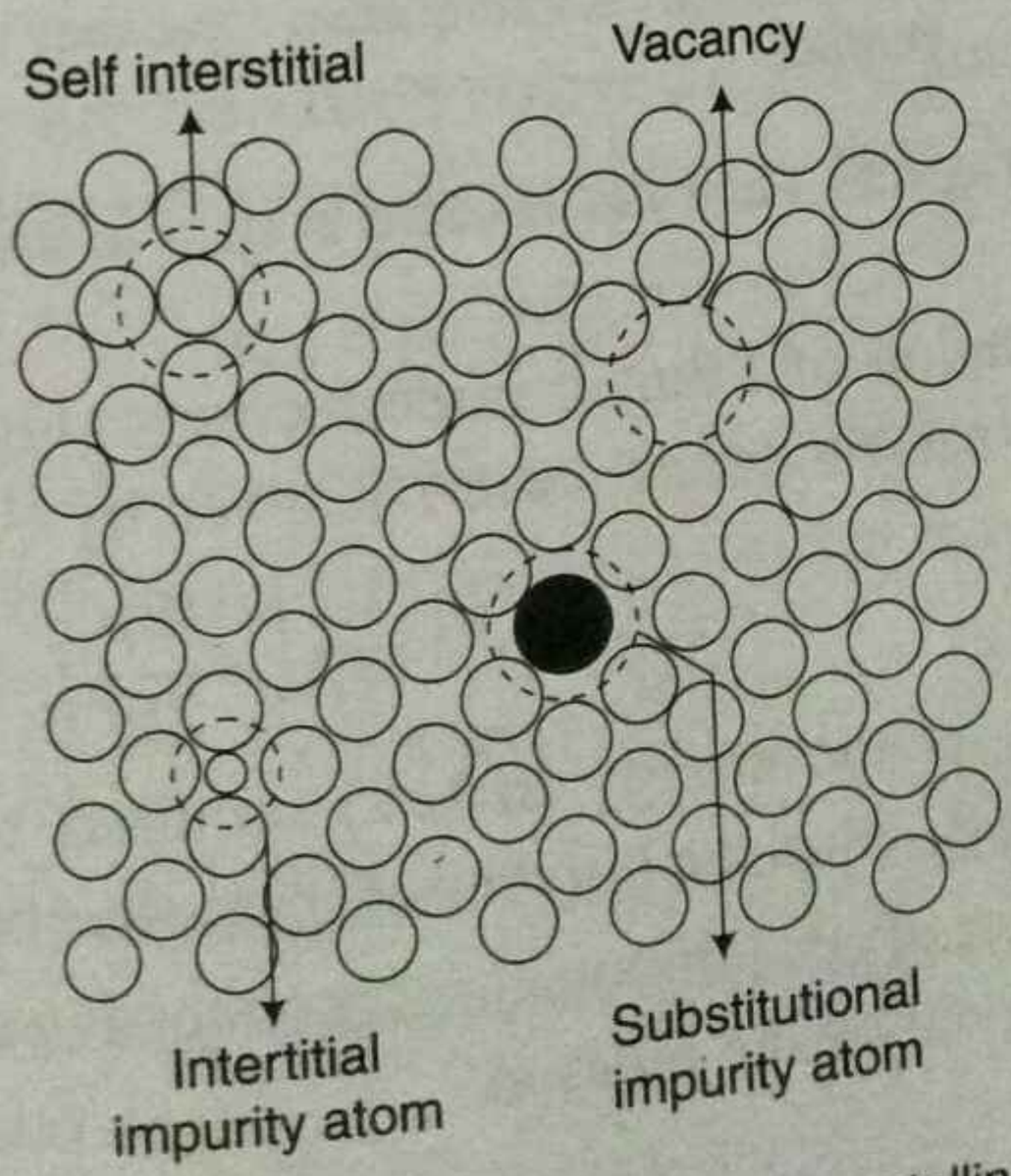


Fig. 4.1 A two-dimensional representation of a simple crystalline solid, illustrating some common point imerfections in metal crystals.

where E_v is the energy (in eV) required to take an atom from the interior to the surface of the crystal, ΔH_f is the energy in kJ/mol and N, k and R respectively are Avogadro's number, Boltzmann constant and gas constant.

(c) Concentration of Schottky imperfections (Fig. 4.2) in an ionic solid (Such as $NaCl$)at a certain temperature T is given by

$$n = N\exp\left(-\frac{E_p}{2kT}\right)$$

where E_p is the energy (in eV) required to remove an ion pair.

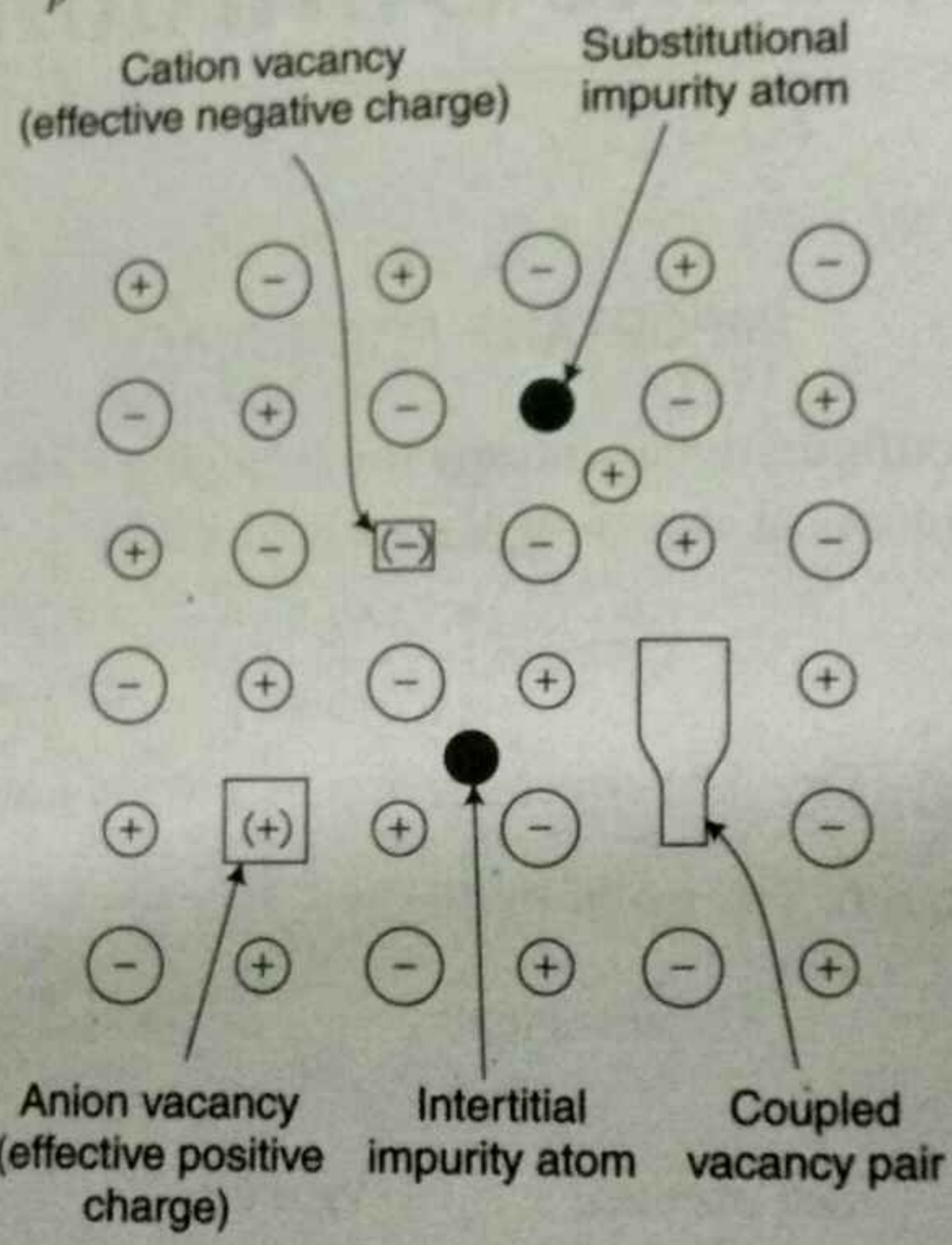


Fig. 4.2 Point imperfections in an ionic solid

(d) Concentration of Frenkel imperfections (Fig. 4.1) in monoatomic solid at a certain temperature T is given by

$$n = (NN_i)^{1/2}\exp\left(-\frac{E_F}{2kT}\right)$$

where E_F is the energy in (eV) required to create one Frenkel imperfection. N_i is the number of interstitial sites in the crystal.

4.2 (a) The number of edge dislocations produced in a curved surface under stress is given by the relation

$$nb = \frac{Lt}{r}$$

where b is the Burgers vector, L is the length of the strip, t is the thikness and r is the radius of curvature produced in the strip.

(b) The density of dislocation in a curved surface under stress is the number of dislocation lines piercing through a unit area of the plane. It is given by

$$\rho = \frac{n}{Lt} = \frac{1}{rb}$$

4.3 (a) The shear stress needed to move a dislocation is given by

$$\tau = \frac{2Gb \sin\theta}{l}$$

where, G is the elastic shear modulus, b is the Burgers vector, l is the distance between a pair of precipitate particles, (obstacles) encountered by dislocation (Fig. 4.3).

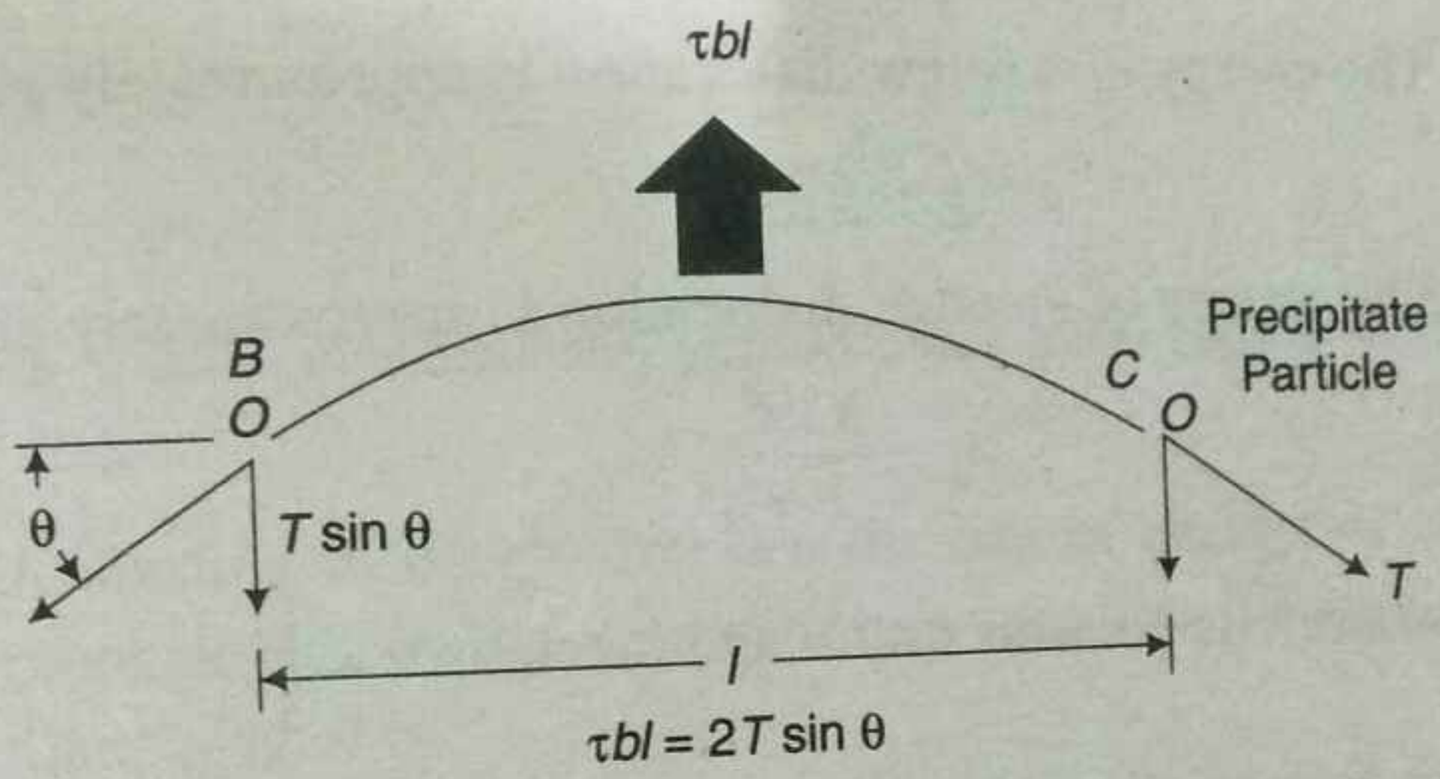


Fig. 4.3 Dislocation line tension when the dislocation encounters the obstacles B and C

(b) The shear stress needed to move a dislocation as calculated by Peirls and Nabarro (in terms of its width) is given by

$$\tau_{PN} = \mu \exp\left(-\frac{2\pi\omega}{b}\right)$$

where μ is the shear modulus and ω is the width of the dislocation.

4.4 (a) The rate of plastic deformation i.e strain rate is given by

$$\dot{\epsilon} = \exp\left(-\frac{Q}{kT}\right)$$

where Q is the activation energy for dislocation motion.

(b) The strain rate can also be expressed in terms of velocity of dislocation v_d as

$$\dot{\epsilon} = \rho b\, v_d$$

where ρ is the density of mobile dislocation

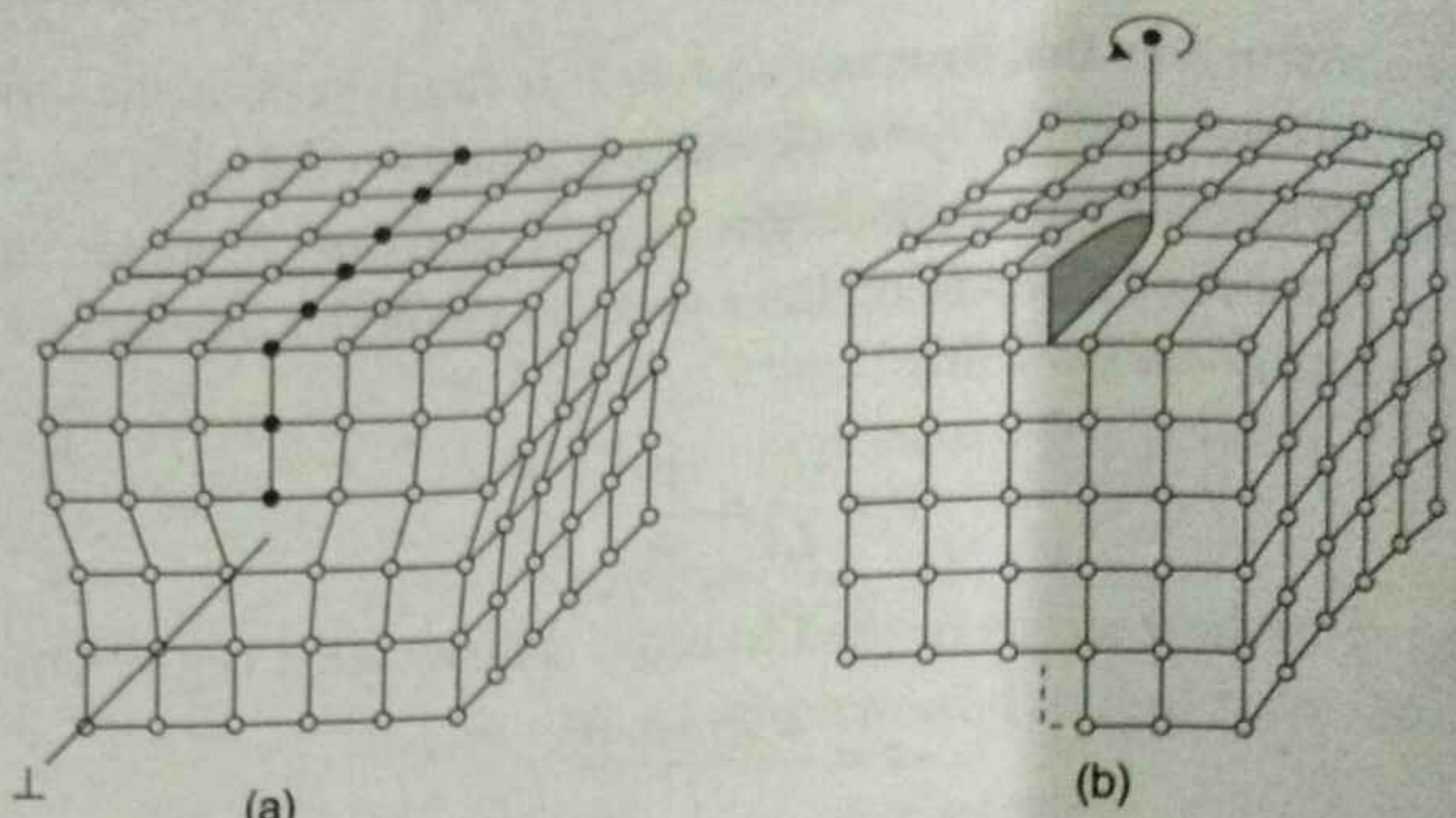


Fig. 4.4 Geometry of simple dislocations. (a) Edge dislocation and (b) screw dislocation. The lines normally used to represent the dislocations are also indicated, as are the symbols for them, ⊥ and ⊙

4.5 (a) The energy of a screw dislocation is approximately given by

$$E \simeq lGb^2$$

(b) The energy of an edge dislocation is approximately given by

$$E \simeq \frac{lGb^2}{1-\nu}$$

where ν is poisson's ratio and taken as $\nu = \frac{1}{3}$.

$\Rightarrow$ Energy of an edge dislocation (Fig. 4.4a) is $\frac{3}{2}$ times that of screw dislocation (Fig. 4.4b) of same length.

(c) The lines tension along a curved dislocation is given by

$$T = \frac{\partial E}{\partial l} = Gb^2$$

4.6 The angle of tilt (θ), the Burgers vector (b) and the average height (h) of an edge dislocation (Fig. 4.5) are related through the equation

$$\tan\theta = \frac{b}{h}$$

For small angle, $\tan\theta \simeq \theta$, therefore, we have

$$\theta \simeq \frac{b}{h}$$

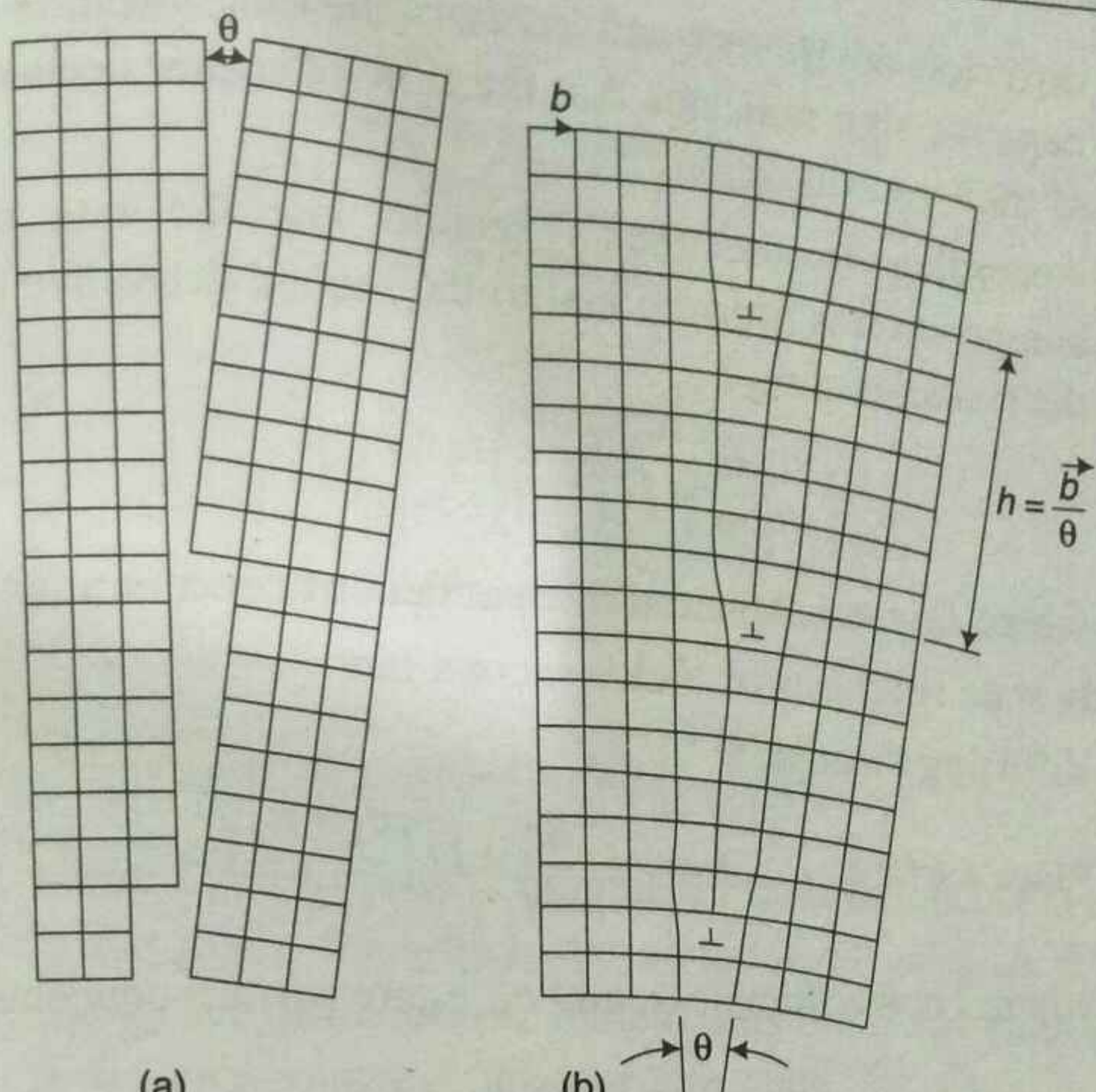


Fig. 4.5 Low-angle tilt boundary envisaged as a line of edge dislocations.

4.7 (a) According to Fick's first law the rate of change of composition is proportional to the concentration. gradient i.e. the flux across a plane (Fig. 4.6),

$$J = \frac{1}{A}\frac{dn}{dt} = -D\left(\frac{dc}{dx}\right)$$

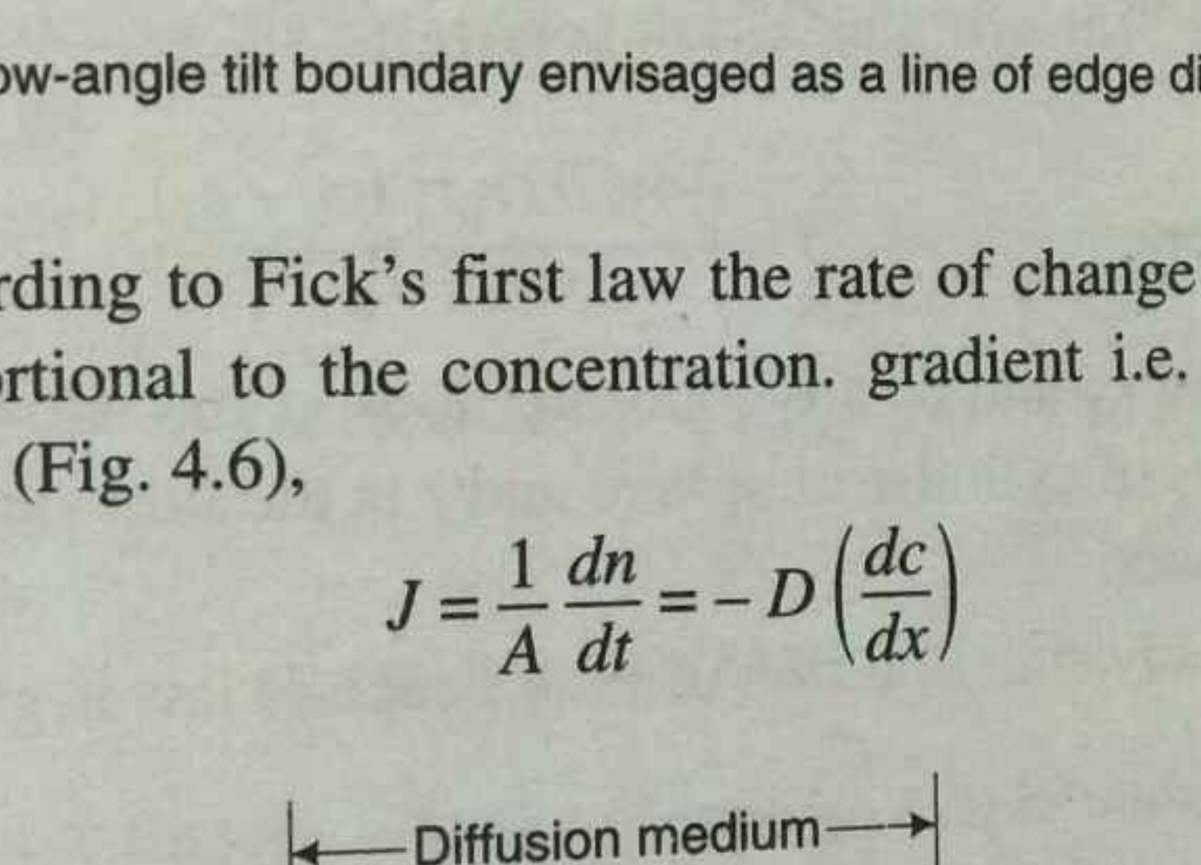


Fig. 4.6 Concentration-distance profile for steady state diffusion

where $\frac{dn}{dt}$ is the number of moles of the diffusing atoms crossing per unit time through a cross sectional plane of area A, D is the

diffusion coefficient and dc/dx is the concentration gradient. The negative sign indicates that the flow of matter occurs from regions of high concentration.

(b) According to the Fick's second law the rate of change of composition is proportional to the second derivative (Laplacian) of the concentration, i.e.

$$\frac{dc}{dt} = D\left(\frac{d^2c}{dx^2}\right)$$

where D is constant and independent of concentration.

4.8 Steady state solutions of Fick's second law

Flux diffusing through a:

(a) Plane surface: $$J = -D\frac{dc}{dx} = D\left(\frac{c_1 - c_2}{l}\right)$$

where l is the thickness, and c_1, c_2 are surface concentrations.

(b) Cylinder: $$J = \frac{-2\pi Dt\,(c_2 - c_1)}{\ln\,(r_1/r_0)}$$

(c) Sphere: $$J = \frac{-4\pi D\,t\,r_0 r_1\,(c_2 - c_1)}{r_1 - r_0}$$

where c_1 and c_2 are concentrations at the two surfaces $r = r_0$ and $r = r_1$ of cylinder or sphere and t is the time during which the flux diffuses.

4.9 Non – steady state solution of Fick's second law is given by

$$\frac{C_s - C_x}{C_s - C_0} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

where C_0 = initial uniform concentration of the element in solid medium

C_s = surface concentration of element in gas diffusing into solid

C_x = concentration of gas at a distance x from the surface at a time t (Fig. 4.7)

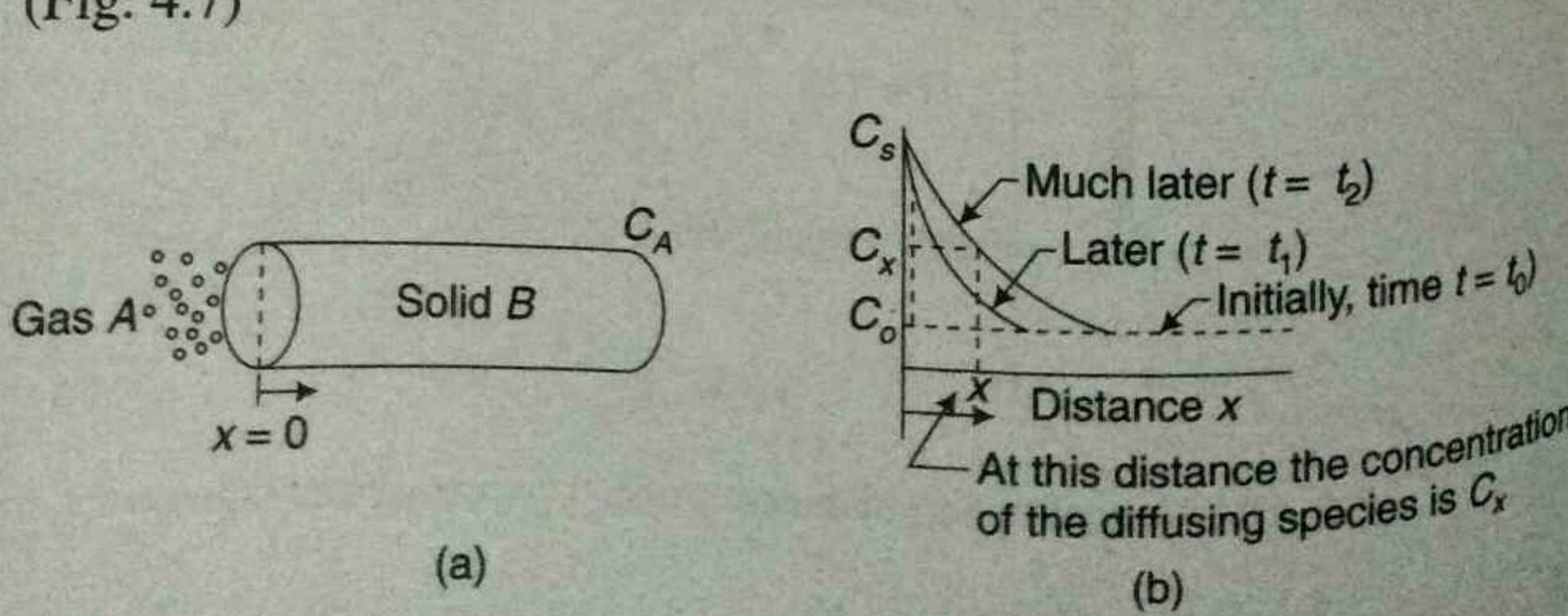


Fig. 4.7 Diffusion of a gas into a solid (a) Gas A diffuse into a solid B and (b) Concentration-distance profiles of element A for different times.

If C_x takes some specific value (say C_1), then

$$\frac{C_s - C_1}{C_s - C_0} = \text{constant}$$

$$\Rightarrow \qquad \frac{x}{2\sqrt{Dt}} = \text{constant}$$

or

$$\frac{x^2}{Dt} = \text{constant}$$

or $x \simeq \sqrt{Dt}$ = diffusion length

4.10 (a) The diffusion co-efficient D of many systems obey Arrhenius type of equation, i.e.

$$D = D_0 \, exp\left(-\frac{E}{kT}\right)$$

where D_0 is a pre-exponential constant independent of temperature in the range for which the equation is valid, E is the activation energy for diffusion (in Joules), k is the Boltzmann constant and T is the temperature in the absolute scale.

(b) In terms of molar and caloric unit the diffusion coefficient is given by

$$D = D_0 \, exp\left(-\frac{Q}{RT}\right)$$

where Q is the activation energy (in cal/mol) and R is a gas constant.

Solved Examples

Example 4.1 Show that the entropy of mixing equal numbers of two different kinds of atoms on one mole of fixed atomic sites is 5.76 J mol^{-1} K^{-1}.

Solution: Given: One mole of fixed atomic sites = $N = 6.023 \times 10^{23}$ mol^{-1}, two equal but different kinds of atoms, i.e., $n = \frac{N}{2}$, $S_{cf} = S_{\text{mixing}}$. Making use of the configurational entropy formula, we can write

$$S_{\text{mixing}} = S_{cf} = k \ln \left[\frac{N!}{(N-n)!\, n!}\right]$$

$$= k\,[N \ln N - (N-n) \ln (N-n) - n \ln n]$$

$$= k \left[N \ln N - \frac{N}{2} \ln \frac{N}{2} - \frac{N}{2} \ln \frac{N}{2}\right]$$

$$= k \left[N \ln N - N \ln \frac{N}{2}\right]$$

$$= kN \left[\ln N - \ln \frac{N}{2}\right]$$

$$= kN\left[\ln N - \ln \frac{N}{2}\right]$$

$$= kN\,[\ln N - \ln N + \ln 2]$$

$$= kN \ln 2$$

$$= 1.380 \times 10^{-23} \times 6.023 \times 10^{23} \times 0.693$$

$$= 5.76 \text{ J mol}^{-1} \text{ K}^{-1}$$

Example 4.2 Calculate the fraction of atoms with energies equal to or greater than 1 eV at 300K and 1500K.

Solution: Given: $E = 1.0$ eV, Temperatures $T_1 = 300$ K and $T_2 = 1500$ K, n/N (at 300 K) = ? n/N (at 1500 K) = ?

We know that the Boltzmann's constant in terms of electron volts is given as

$$k = 8.614 \times 10^{-5} \text{ eV/K}$$

Now, making use of the formula

$$\frac{n}{N} = \exp\left(-\frac{E}{kT}\right)$$

We can obtain the fraction of atoms at 300 K,

$$\frac{n}{N} = \exp\left(-\frac{1}{8.614 \times 10^{-5} \times 300}\right)$$

$$= \exp(-38.697)$$

$$= 1.56 \times 10^{-17}$$

Similarly at 1500 K,

$$\frac{n}{N} = \exp\left(-\frac{1}{8.614 \times 10^{-5} \times 1500}\right)$$

$$= \exp(-7.739)$$

$$= 4.35 \times 10^{-4}$$

Example 4.3 Calculate the ratio of the number of vacancies in equilibrium at 300 K in aluminium to that produced by rapid quenching from 800 K.

Solution: Given: Temperatures $T_1 = 300$ K, $T_2 = 800$ K, material is Aluminium, $\frac{n_{300}}{n_{800}} = ?$

Refer Table 4.1 enthalpy of formation of vacancy for Al is given as 0.7 eV/vacancy. Therefore, at 300 K,

$$n_{300} = N \exp\left(-\frac{0.7}{8.614 \times 10^{-5} \times 300}\right)$$

$$= N \exp(-27.088) = N \times 1.7217 \times 10^{-12}$$

Similarly at 800 K,

$$n_{800} = n \exp\left(-\frac{0.7}{8.614 \times 10^{-5} \times 800}\right)$$

$$= N \exp(-10.158)$$

$$= N \times 3.8769 \times 10^{-5}$$

so that $$\frac{n_{300}}{n_{800}} = \frac{N \times 1.7217 \times 10^{-12}}{N \times 3.8769 \times 10^{-5}}$$

$$= 4.44 \times 10^{-8}$$

Table 4.1 Enthalpy of formation of vacancies in some crystals

Crystal	Kr	Cd	Pb	Zn	Mg	Al	Ag	Cu	Ni
ΔH_f kJ mol^{-1} 7.7	38	48	49	56	68	106	120	168	
eV/vacancy	0.08	0.39	0.50	0.51	0.58	0.70	1.10	1.24	1.74

Example 4.4 The energy of formation of a vacancy in copper is 1 eV. Estimate the relative change in the density of copper due to vacancy formation at a temperature just below its melting point, 1356 K.

Solution: Given: $E_v = 1$ eV, $T = 1356$K, $k = 8.614 \times 10^{-5}$ eV/K, relative change in the density of cu = ?

Making use of the equation of vacancy concentration in a monoatomic solid containing only the configuration entropy term, we have

$$\frac{n}{N} = \exp\left(-\frac{E_v}{kT}\right) = \exp\left(-\frac{1}{8.614 \times 10^{-5} \times 1356}\right)$$

$$= \exp(-8.56)$$

$$= 1.914 \times 10^{-4}$$

Therefore, the number of vacancy per mole is

$$n = 6.023 \times 10^{23} \times 1.914 \times 10^{-4}$$

$$= 1.1528 \times 10^{20}$$

Now, the change in the density of copper due to vacancy formation is

$$n + N = 6.0241528 \times 10^{23}$$

Therefore, the relative change in the density of copper due to vacancy formation is

$$\frac{n+N}{N} = 1.0001914:1$$

Example 4.5 The concentration of Schottky defects in a *fcc* crystal is 1 in 10^{10} at 300 K. Estimate the value of concentration to be expected at 1000 K.

Solution: Given: $(n:N)_{300\,K} = 1:10^{10}$, $T_1 = 300$ K, $T_2 = 1000$ K, $(n:N)_{1000\,K} = ?$

Since $\frac{n}{N} = \frac{1}{10^{10}} = 10^{-10} = \exp(-10 \times 2.303) = \exp(-23.03)$

$$= \exp\left(-\frac{E_v}{kT}\right)$$

$$\Rightarrow \qquad 23.03 = \frac{E_v}{kT}$$

or $$E_v = 23.03 \times kT$$
$$= 23.03 \times 8.614 \times 10^{-5} \times 300$$
$$= 0.595 \text{ eV}$$

Therefore, the defect concentration at 1000 K is

$$\frac{n}{N} = \exp\left(-\frac{E_v}{kT}\right)$$
$$= \exp\left(-\frac{0.595}{8.614 \times 10^{-5} \times 10^3}\right)$$
$$= \exp(-6.909)$$
$$= 9.987 \times 10^{-4}$$
$$\simeq 10^{-3}$$

$$\Rightarrow \qquad n:N = 1:10^3$$

Example 4.6 The energy required to remove a pair of ions, Na^+ and Cl^-, from NaCl is ~ 2 eV. Calculate the number of Schottky imperfections present in the NaCl crystal at 300 K.

Solution: Given: $E_p = 2$ eV, $T = 300$ K, $n = ?$

Using the expression

$$\frac{n}{N} = \exp\left(-\frac{E_p}{2kT}\right)$$
$$= \exp\left(-\frac{2}{2 \times 8.614 \times 10^{-5} \times 300}\right)$$
$$= \exp(-38.70)$$
$$= 1.564 \times 10^{-17}$$

or $$n = 6.023 \times 10^{23} \times 1.564 \times 10^{-17}$$
$$= 9.42 \times 10^6$$

Now, since the volume of one mole of the crystal = 26.83 cm^3,

Therefore, $$n = \frac{9.42 \times 10^6}{26.83} = 0.35 \times 10^6 \text{ cm}^{-3}$$

Example 4.7 The density of Schottky defects in a certain sample of sodium chloride is 5×10^{11} m^{-3} at 300 K. If the interionic separation is 2.82 Å, what is the average energy required to create one Schottky defect?

Solution: Given: Density of Schottky defects, $n = 5 \times 10^{11}$ m^{-3}, $T = 300$ K, interionic separation $= 2.82$ Å $= 2.82 \times 10^{-10}$ m, $E_p = ?$

Volume of one unit cell of NaCl,

$$V = a^3 = (2R)^3$$
$$= (2 \times 2.82 \times 10^{-10})^3$$
$$= 1.794 \times 10^{-28} \text{ m}^3$$

Since the unit cell of NaCl (without defect) contains 4 ion pairs, therefore, the number of ion – pairs contained in 1 m^3 of an ideal NaCl crystal is

$$N = \frac{4}{1.794 \times 10^{-28}} = 2.23 \times 10^{28} \text{ ion pairs.}$$

Now, using the expression

$$\frac{n}{N} = exp\left(-\frac{E_p}{2kT}\right), \text{ we obtain}$$

$$E_p = 2kT \times \ln\left(\frac{N}{n}\right)$$

$$= 2 \times 8.614 \times 10^{-5} \times 300 \times \ln\left(\frac{2.23 \times 10^{28}}{5 \times 10^{11}}\right)$$

$$= 1.98 \text{ eV}$$

Example 4.8 Show that the number of Frenkel defects in equilibrium at a given temperature is given by

$$n = (NN_i)^{1/2} \, exp\left(-\frac{E_F}{2kT}\right)$$

where N is the total number of atoms in the system, N_i is the number of interstitial atoms and E_F is the energy required to displace an atom from a regular site to an interstitial site.

Given: N = total number of atoms (lattice sites) in the system, N_i = the interstitial number of atoms, E_F = the energy required to create one Frenkel defect.

Proof: Let us consider a monoatomic solid. In order to create n Frenkel defects, we displace n atoms from their regular atomic sites to the interstitial sites. Then the number of ways of arranging n identical vacancies and $(N-n)$ identical atoms on N sites is

$$\frac{N!}{(N-n)!\,N!}$$

Also the number of ways of arranging n identical vacancies and $(N_i - n)$ identical atoms on N_i identical sites is

$$\frac{N_i!}{(N_i-n)!\,n!}$$

so that the total probability of creating n Frenkel defects will become

$$W = \frac{N!}{(N-n)!\,n!} \times \frac{N_i!}{(N_i-n)!\,n!}$$

The corresponding change in the entropy associated due to the creation of n Frenkel defects is given by

$$S = k \ln W = k \ln \left[\frac{N!}{(N-n)!\,n!} \times \frac{N_i!}{(N_i-n)!\,n!} \right]$$

where k is the Boltzmann constant. This in turn produces a change in the free energy of the system, i.e.

$$F = E - TS$$

or

$$F = nE_F - k \ln \left[\frac{N!}{(N-n)!\,n!} \times \frac{N_i!}{(N_i-n)!\,n!} \right] \quad (1)$$

The logarithmic terms can be solved by using stirling's approximation,

$$\ln x! \cong x \ln x - x \quad \text{for } x >> 1$$

so that

$$\ln \left[\frac{N!}{(N-n)!\,n!} \times \frac{N_i!}{(N_i-n)!\,n!} \right] = \ln \left[\frac{N!}{(N-n)!\,n!} \right] + \ln \left[\frac{N_i!}{(N_i-n)!\,n!} \right]$$

$$= N \ln N - (N-n) \ln (N-n) - n \ln n + N_i \ln N_i - (N_i-n) \ln (N_i-n) - n \ln n$$

$$= N \ln N + N_i \ln N_i - (N-n) \ln (N-n) - (N_i-n) \ln (N_i-n) - 2n \ln n$$

When the equilibrium is reached at a given temperature, there is no further change in the free energy of the system. After substituting the value of logarithmic term in eq. 1, differentiate it w.r.t n. At equilibrium, we obtain

$$\left(\frac{\partial f}{\partial n} \right)_T = E_F - kT \ln \left[\frac{(N-n)\,(N_i-n)}{n^2} \right] = 0$$

or

$$E_F = kT \ln \left[\frac{(N-n)\,(N_i-n)}{n^2} \right]$$

If $n << N$ and $n << N_i$, then

$$E_F \simeq kT \ln \left(\frac{NN_i}{n^2} \right)$$

$$= kT \ln (NN_i) - 2 \ln n$$

or

$$\ln n = \frac{1}{2} \ln (NN_i) - \frac{E_F}{2kT}$$

or

$$n = (NN_i)^{1/2} \exp \left(-\frac{E_F}{2kT} \right)$$

Example 4.9 The average energy required to create a Frenkel defect in an ionic crystal $A^{2+}B^{2-}$ is 1.4 eV. Calculate the ratio of Frenkel defects at 300 K and 600 K in 1 gm of crystal material.

Solution: Given: $E_F = 1.4$ eV, $T_1 = 300$ K, $T_2 = 600$ K, $\left(\frac{n_{300}}{n_{600}}\right)$ using the expression $n = (NN_i)^{1/2} \exp\left(-\frac{E_F}{2kT}\right)$, we obtain

$$n_{300} = (NN_i)^{1/2} \exp\left(-\frac{1.4}{600\ \text{k}}\right)$$

and

$$n_{600} = (NN_i)^{1/2} \exp\left(-\frac{1.4}{1200\ \text{k}}\right)$$

so that

$$\frac{n_{300}}{n_{600}} = \exp\left(-\frac{1.4}{\text{k}}\right)\left(\frac{1}{600} - \frac{1}{1200}\right)$$

$$= \exp\left(-\frac{1.4}{8.614 \times 10^{-5}}\right) \times \frac{1}{1200}$$

Simplifying this, we obtain

$$\frac{n_{300}}{n_{600}} = 1.316 \times 10^{-6}$$

Example 4.10 In a simple cubic crystal ($a = 3$ Å), a positive edge dislocation 1 mm long climbs up by 1 μm. How many vacancies are lost or created?

Solution: Given: A cubic crystal with $a = 3$ Å $= 3 \times 10^{-10}$ m, dislocation length $= 1$ mm $= 10^{-3}$ m, distance of dislocation climb is 1 μm $= 10^{-6}$ m, Number of vacancies lost or created = ?

Consider the case shown in Fig. 4.8 when the dislocation climbs up, vacancies are lost. The affected area in this case is

$$10^{-3}\ \text{m} \times 10^{-6}\ \text{m} = 10^{-9}\ \text{m}^2$$

Since the area of the unit cell is 9×10^{-20} m^2 and the number of atoms in the unit cell in a simple cubic crystal is 1. Therefore, the number of vacancies lost from the affected area is

$$\frac{1 \times 10^{-9}}{9 \times 10^{-20}} = 1.1 \times 10^{10} \text{ lost}$$

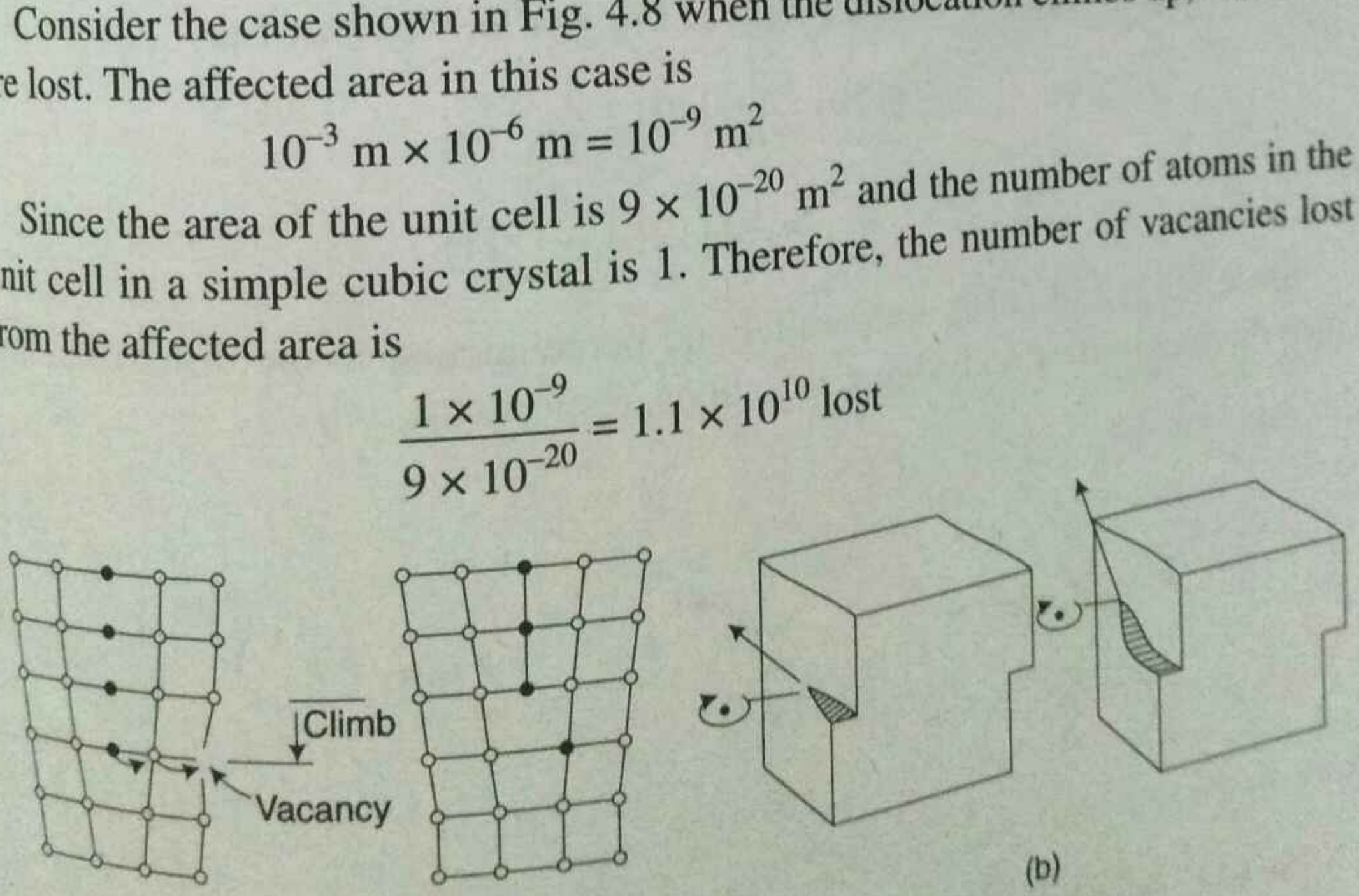


Fig. 4.8 (a) Climb of an edge dislocation (b) cross-slip of a screw dislocation

Example 4.11 The Burgers vector of a mixed dislocation line is 1/2 $[\bar{1}10]$. The dislocation line lies along the $[\bar{1}12]$ direction. Find the slip plane on which this dislocation lies. Find also the screw and the edge components of the Burgers vector.

Solution: Given: Burgers vector of a mixed dislocation = 1/2 $[\bar{1}10]$, direction of dislocation line = $[\bar{1}12]$, slip plane =? Burgers vector of screw dislocation =? Burgers vector of edge dislocation =? ·

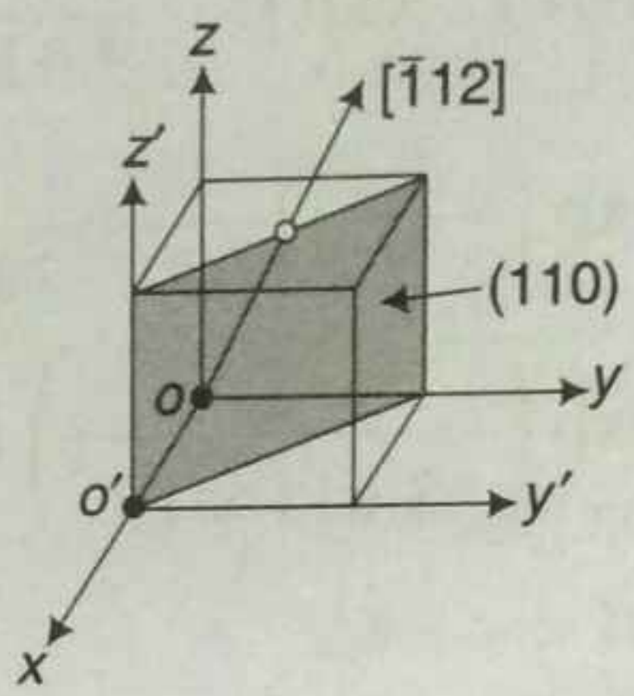


Fig. 4.9 Showing dislocation line and slip plane

We know that the Burgers vector of an edge dislocation and the dislocation line define the slip plane. This implies that they must lie in the same slip plane. Now from the Fig. 4.9, we find that the required plane containing the Burgers vector and the dislocation line is (110). Also keeping in view the fact that in edge dislocation the Burgers vector is perpendicular to the dislocation line and in screw dislocation it is parallel. With the help of Fig. 4.10*a*, we can write

$$\frac{1}{2}[\bar{1}10] = \frac{1}{6}[\bar{1}12] + \frac{1}{6}[\bar{2}2\bar{2}]$$

$$= \frac{1}{6}[\bar{1}12] + \frac{1}{3}[\bar{1}1\bar{1}]$$

Since $[\bar{1}12]$ and $[\bar{1}1\bar{1}]$ are parallel and perpendicular to the dislocation line, they represent screw and edge dislocations, respectively.

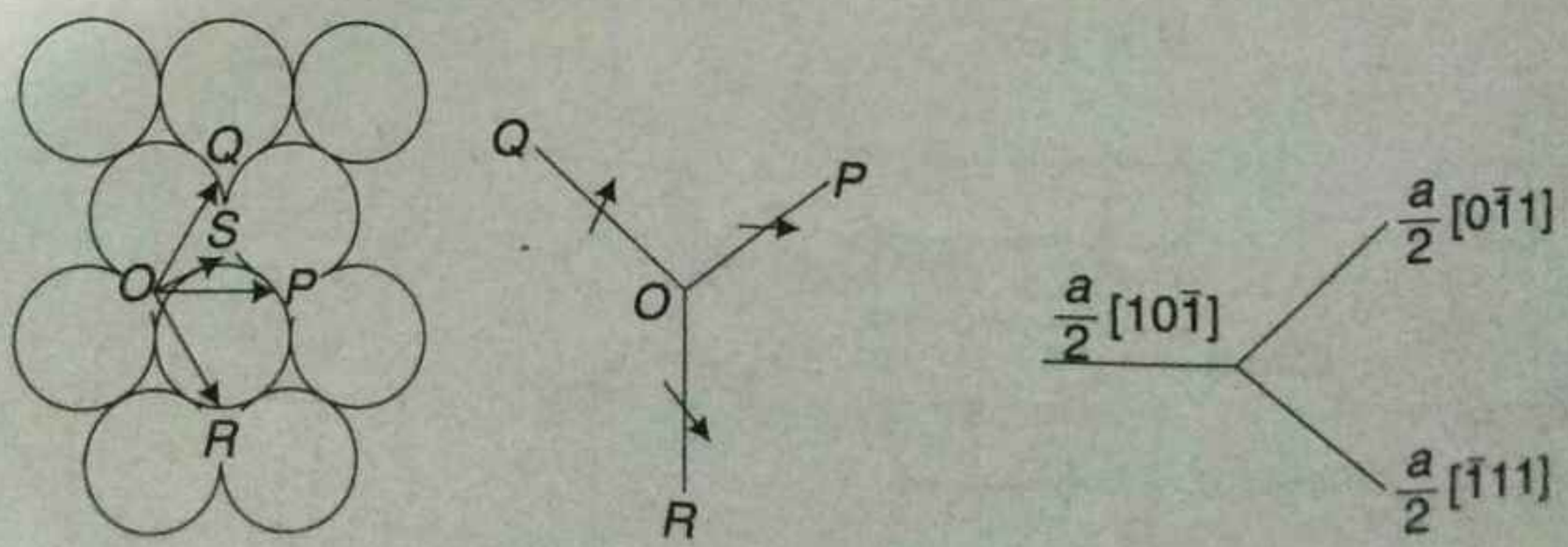


Fig. 4.10 Burgers vectors (a) On a close packed plane (b) meeting at a dislocation node

Example 4.12 A copper crystal has a dislocation density of 1.0×10^{13} m^{-2}. The shear modulus of copper is 44 MN m^{-2}. Calculate the elastic energy of line imperfection stored in the crystal.

Solution: Given: Crystal of copper with $\tau = 1.0 \times 10^{13}$ m^{-2}, $\mu = 44$ MNm^{-2}, elastic energy = ?

For Cu, $a = 3.61$ Å $= 3.61 \times 10^{-10}$ m. Since Cu has *fcc* structure, the Burgers vector, $b = \frac{a}{2}[110]$ is

$$b = \frac{a}{\sqrt{2}} = \frac{3.61}{\sqrt{2}}$$

$$= 2.55 \text{ Å}$$

$$= 2.55 \times 10^{-10} \text{m}$$

Now, the elastic energy per unit length of dislocation is

$$E = \frac{\mu b^2}{2} = \frac{44 \times 10^6 \times (2.55 \times 10^{-10})^2}{2}$$

$$= 14.30 \times 10^{-13} \text{ Jm}^{-1}$$

Therefore, the elastic energy stored in the crystal is

$$E\tau = 14.30 \times 10^{-13} \times 1.0 \times 10^{13}$$

$$= 14.30 \text{ Jm}^{-3}.$$

Example 4.13 Show both graphically and analylitically that the first two dislocations add to give the third dislocation in the following reaction

$$\frac{1}{6}[21\bar{1}] + \frac{1}{6}[121] \rightarrow \frac{1}{2}[110]$$

Solution: Given:

$$\frac{1}{6}[21\bar{1}] + \frac{1}{6}[121] \rightarrow \frac{1}{2}[110]$$

The above reaction shows that two partial dislocations combine and form a unit dislocation (Fig. 4.10). Using $a/6$ as the unit length, the above reaction can be written in a more simplified form as

$$[21\bar{1}] + [121] \rightarrow [330]$$

This is more clear and helps us to verify that

$$\frac{1}{6}[2+1, 1+2, \bar{1}+1] = \frac{1}{2}[110]$$

Example 4.14 Calculate the square of the Burgers vector of the above dislocations and determine whether the reactions from left to right is energetically favoured.

Solution: Given:

$$\frac{1}{6}[21\bar{1}] + \frac{1}{6}[121] \rightarrow \frac{1}{2}[110]$$

We know that the energy of a dislocation is given by $E \simeq lGb^2$, where l (dislocation line) and G (elastic moduli) are constants for a given dislocation. Now, squaring the length of the Burgers vectors of both sides, we obtain,

$$(\text{length})^2_{[21\bar{1}]} = (2)^2 + (1)^2 + (-1)^2 = 6$$

$$(\text{length})^2_{[121]} = (1)^2 + (2)^2 + (1)^2 = 6$$

$$(\text{length})^2_{[110]} = (1)^2 + (1)^2 + (0)^2 = 2$$

Therefore, the relative energies are

$$\frac{\text{Energy of two partial dislocations}}{\text{Energy of one perfect dislocation}} = \frac{lG\left[\frac{1}{6^2} \times 6 + \frac{1}{6^2} \times 6\right]}{lG\left[\frac{1}{2^2} \times 2\right]}$$

$$= \frac{1/3}{1/2} = 0.66$$

From the above calculation it is clear that the partial dislocations have less energy (although they have greater total length of Burgers vector. This is in contradiction with the Frank's condition

$$b_1^2 + b_2^2 > b_3^2$$

Therefore, the given reaction is energetically not feasible.

Example 4.15 The interfaces between three phases α, β and γ meet along an edge. The angles subtended at the edge by the three phases are respectively 120°, 105° and 135°. If the surface energy of the $\alpha - \beta$ boundary is 1.00 Jm^{-2}, find the surface energy of $\beta - \gamma$ and $\gamma - \alpha$ interfaces.

Solution: Given: $\alpha = 120°$, $\beta = 105°$ and $\gamma = 135°$, interfacial angle between three phases, $\gamma - \beta$ interface energy $\gamma_{\alpha\beta} = 100$ Jm^{-2}, other two interfacial energies are to be determined

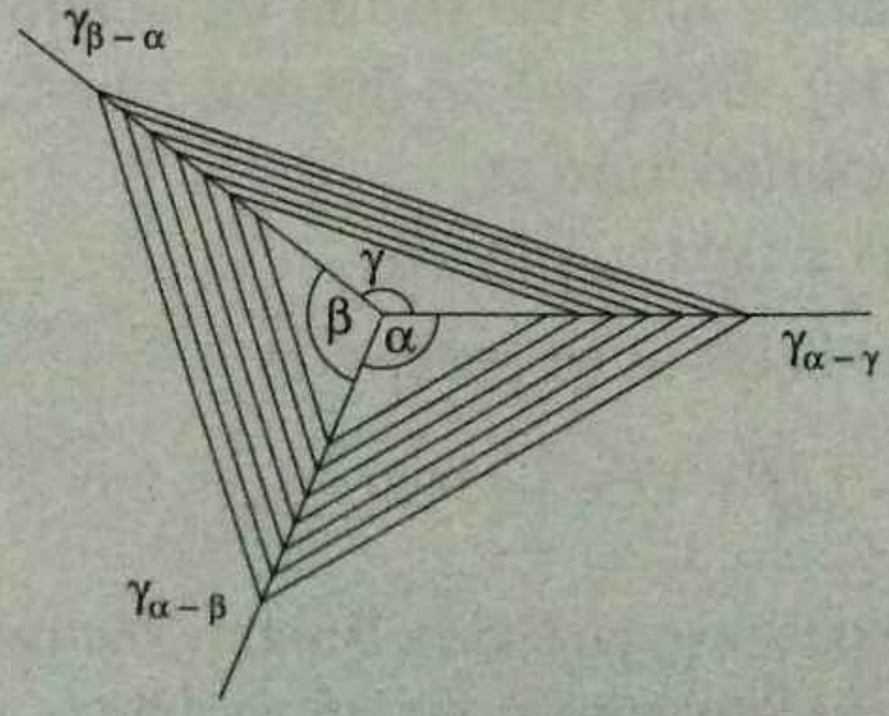


Fig. 4.11 Showing three phases in equilibrium

The given interfacial angles are shown in Fig. 4.11. Three phases are in equilibrium. We know that such surface energies are equivalent to surface tension and hence the above system can be treated as equilibrium of forces, so that,

$$\frac{\gamma_{\alpha\beta}}{\sin 135} = \frac{\gamma_{\beta\gamma}}{\sin 120} = \frac{\gamma_{\gamma\alpha}}{\sin 105}$$

or
$$\frac{1}{0.707} = \frac{\gamma_{\beta\gamma}}{0.866} = \frac{\gamma_{\gamma\alpha}}{0.966}$$

Therefore, we have
$$\gamma_{\beta\gamma} = \frac{0.866}{0.707} = 1.225 \text{ Jm}^{-2}$$

and
$$\gamma_{\gamma\alpha} = \frac{0.966}{0.707} = 1.366 \text{ Jm}^{-2}.$$

Example 4.16 Calculate the spacing between dislocation in a tilt boundary in *fcc* copper crystal, when the angle of tilt is 10° (Burgers vector = 2.6 Å).

Solution: Given: Crystal is *fcc* copper with Burgers vector $b = 2.6$ Å, $\theta = 10°$

using the equation $\tan\theta = \frac{b}{h}$, we have

$$h = \frac{b}{\tan\theta} = \frac{2.6}{\tan 10°} = 14.75 \text{ Å}$$

Example 4.17 The Burgers vector of a mixed dislocation line is 1/2 $[0\bar{1}1]$. The dislocation line lies along the $[2\bar{1}1]$ direction. Find the slip plane on which this dislocation lies Find also the screw and edge components of the Burgers vector.

Solution: Given: Burgers vector of a mixed dislocation = $\frac{1}{2}[0\bar{1}1]$, direction of dislocation line = $[2\bar{1}1]$, slip plane = ?, Burgers vector of edge dislocation = ?, Burgers vector of screw dislocation = ?

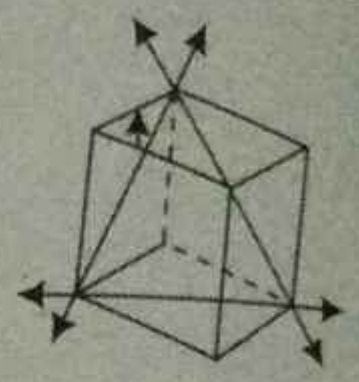
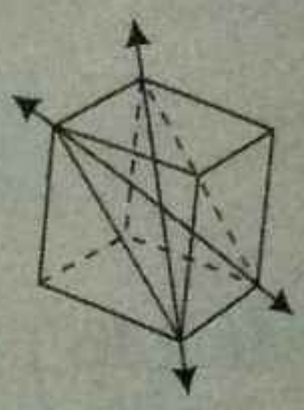
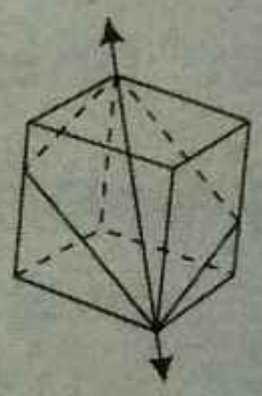
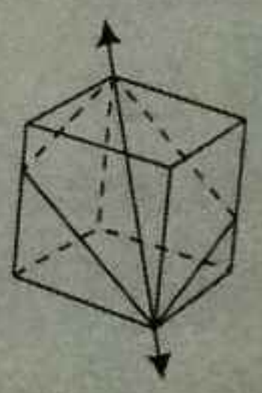
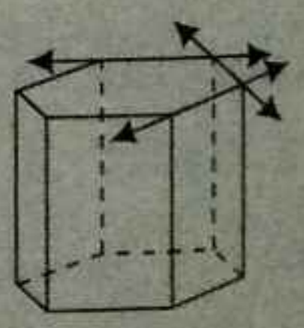
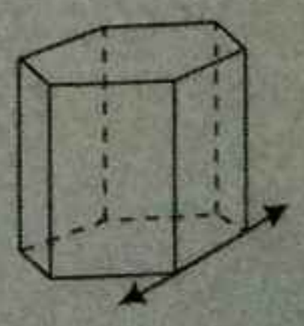
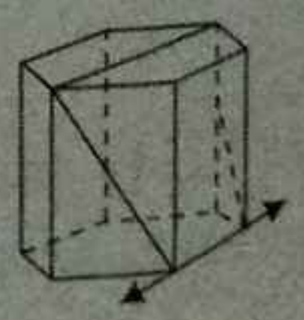
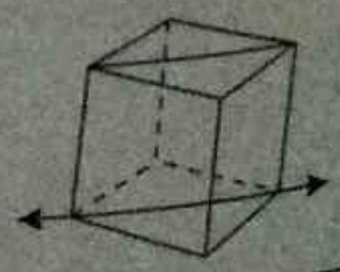
From Fig. 4.12, we find that the required plane containing the Burgers vector is (111). Also keeping in view the fact that in edge dislocation, the Burgers vector is perpendicular to the dislocation line and in screw dislocation it is parallel. With the help of Fig. 4.10, we can write

$$\frac{1}{2}[0\bar{1}1] = \frac{1}{6}[2\bar{1}1] + \frac{1}{6}[\bar{2}\bar{2}2]$$

$$= \frac{1}{6}[2\bar{1}1] + \frac{1}{3}[\bar{1}\bar{1}1]$$

Since $[2\bar{1}1]$ and $[\bar{1}\,\bar{1}1]$ are parallel and perpendicular to the dislocation line, they represent screw and edge components of the dislocation, respectively.

Table 4.2 Observed slip systems in Crystals

Structure	*Slip plane*	*Slip direction*	*No. of slip systems*	*Pictorial view of slip system*
FCC Cu, Al, Ni, Pb, Au, Ag, γFe, ...	{111}	$< 1\bar{1}0 >$	$4 \times 3 = 12$	
Bcc αFe, W, Mo, βBrass	{110}	$< \bar{1}11 >$	$6 \times 2 = 12$	
αFe, Mo, W, Na	{211}	$< \bar{1}11 >$	$12 \times 1 = 12$	
αFe, K	{321}	$< \bar{1}11 >$	$24 \times 1 = 24$	
HCP Cd, Zn, Mg, Ti, Be,...	(0001)	$< 11\bar{2}0 >$	$1 \times 3 = 3$	
Ti	{10$\bar{1}$0}	$< 11\bar{2}0 >$	$3 \times 1 = 3$	
Ti, Mg	{10$\bar{1}$1}	$< 11\bar{2}0 >$	$6 \times 1 = 6$	
NaCl, AgCl	{110}	$< 1\bar{1}0 >$	$6 \times 1 = 6$	

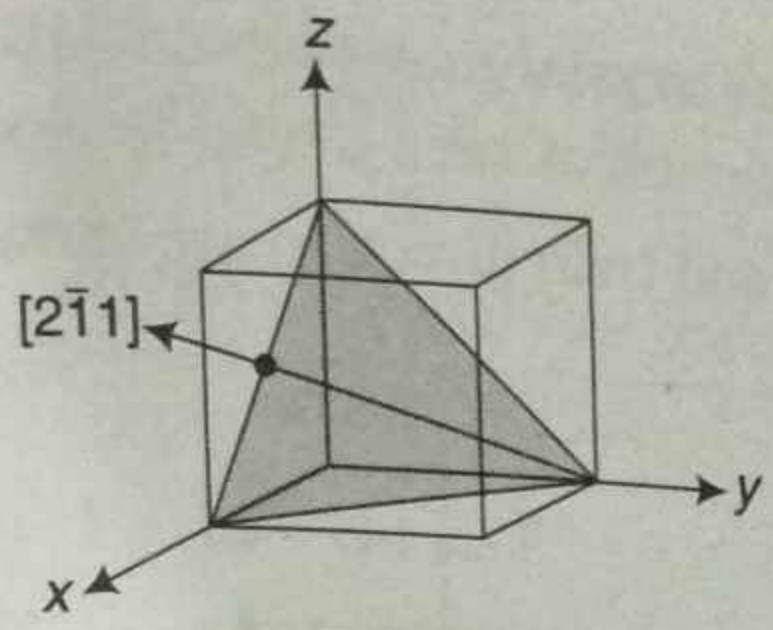


Fig. 4.12 Showing dislocation line and slip plane

Example 4.18 Although Mgo (NaCl crystal structure) is *fcc*, slip in it occurs primarily on {110} <110> rather than on {111} <110> as in *fcc* metal. Sketch a {110} palne and a <110> direction lying in it.

[110] or [$\bar{1}\,\bar{1}$0] direction is shown to lie in ($\bar{1}$10) plane in Fig. 4.13.

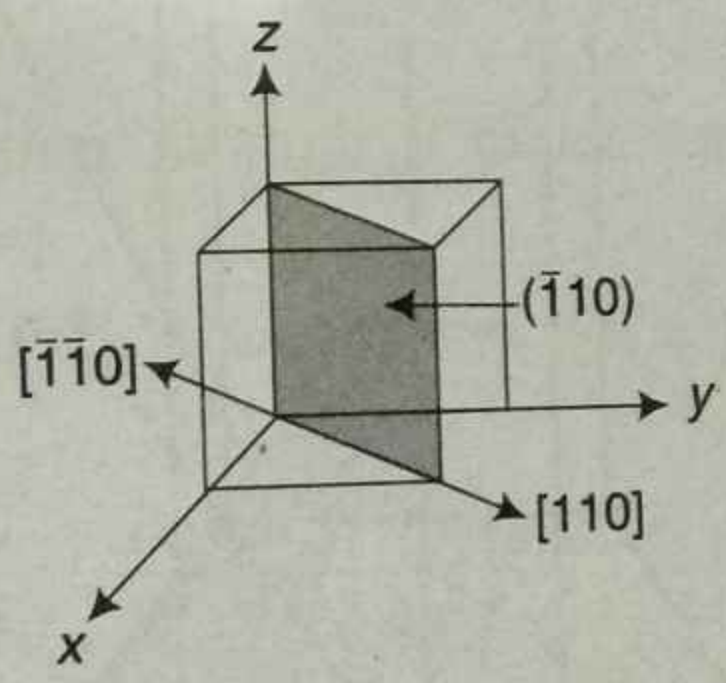


Fig. 4.13 Showing dislocation line and slip plane

Example 4.19 Cadmium slips on {0002} in <11$\bar{2}$0> directions, how many slip systems does it have. Titanium slips on {10$\bar{1}$1} in <11$\bar{2}$0> directions; how many slip systems does it have?

Solution: Given: (i) for cadmium, the slip plane is {0002} and slip direction is <11$\bar{2}$0>, slip system = ?

From Table 4.2, we observe that there is only one (0002) plane and 3 directions of the type [11$\bar{2}$0]. Thus, there are $1 \times 3 = 3$ slip systems.
They are: [11.0] (0002), [$\bar{1}$1.0] (0002) and [1$\bar{1}$,0] (0002).

(ii) For Titanium, the slip plane is {10$\bar{1}$1} and slip direction is <11$\bar{2}$0>. Slip system = ?

From Table 4.2, we observe that there are six such planes but only one direction. Therefore, there are in all $6 \times 1 = 6$ slip systems. They are:

[11$\bar{2}$0] (10$\bar{1}$1), [11$\bar{2}$0] ($\bar{1}$011), [11$\bar{2}$0] (0$\bar{1}$11), [11$\bar{2}$0] (01$\bar{1}$1), [11$\bar{2}$0] ($\bar{1}$101), [11$\bar{2}$0] (1$\bar{1}$01)

Example 4.20 Hexagonal crystal may twin on $\{10\bar{1}2\}$ planes and in $<10\bar{1}1>$ directions. Sketch a cross-section of such a twin in hexagonal Bravais lattice.

The required twin plane and twin direction are shown in Fig. 4.14

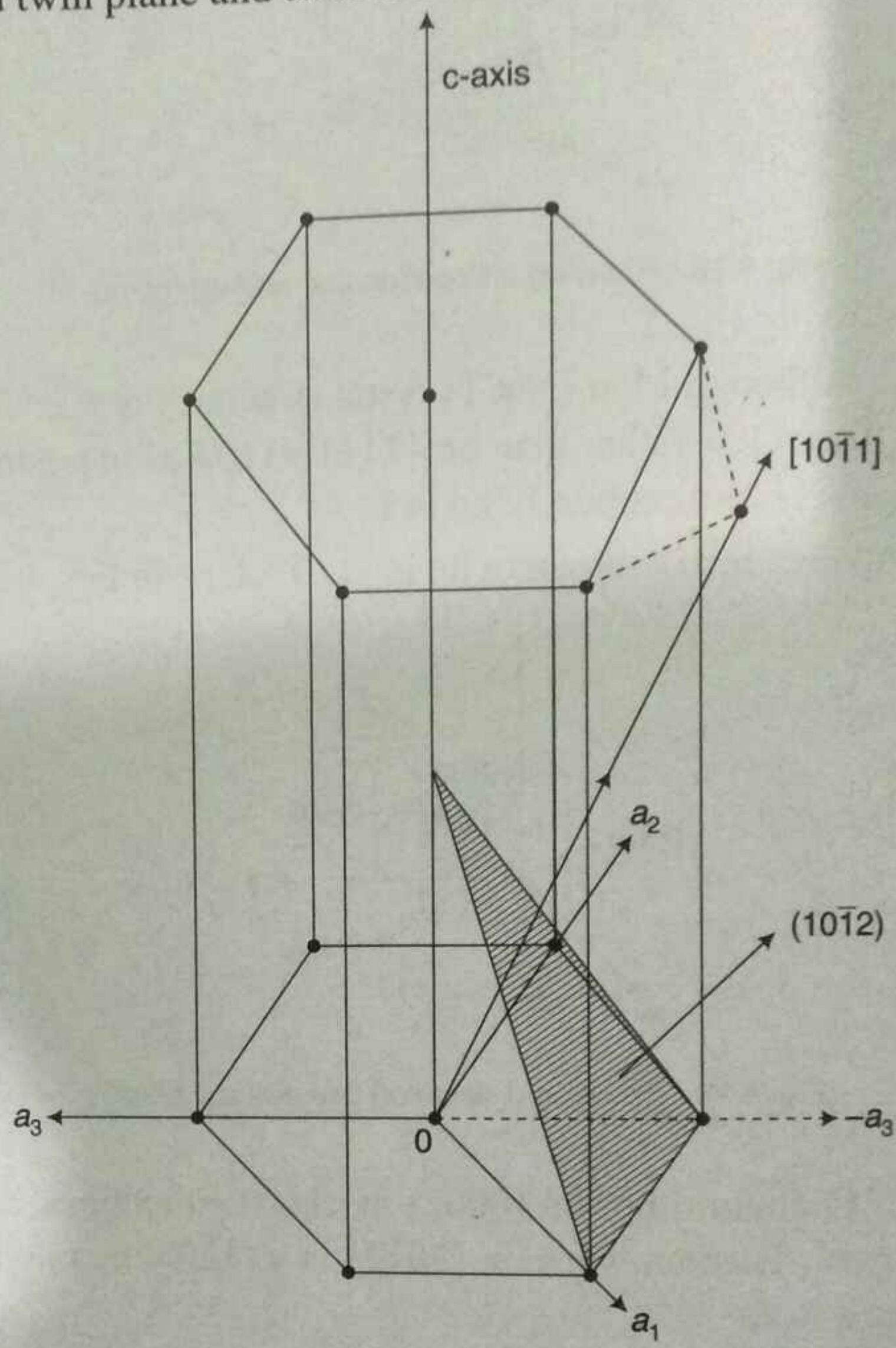


Fig. 4.14 Showing (10$\bar{1}$2) plane and [10$\bar{1}$1] direction in a hexagonal unit cell.

Example 4.21 In a pure thick aluminium sheet, there are 0.19 atomic percent of copper at a surface and 0.18 atomic percent at the depth of 1.2 mm from the surface. Calculate the flux of the copper atom from the surface at 550°C if the diffusion coefficient of copper in aluminium at this temperature is $5.25 \times 10^{-13} m^2 s^{-1}$.

Solution: Given: $c_2 = 0.18 = 0.0018$ per unit volume

$c_1 = 0.19 = 0.0019$ per unit volume

$dx = 1.2$ mm $= 0.0012$m

and $D = 5.25 \times 10^{-13} m^2 s^{-1}$

Since aluminium is *fcc* crystal with lattice parameter $a = 4.05$ Å $= 4.05 \times 10^{-10}$m.

Therefore, the number of aluminium atoms per unit volume is

$$\frac{\text{Atoms}}{m^3} = \frac{4}{(4.05 \times 10^{-10})^3} = 6 \times 10^{28}\ m^{-3}$$

Therefore,

$$\left(\frac{dc}{dx}\right)_{cu} = \frac{(0.0018 - 0.0019) \times 6 \times 10^{28}}{0.0012}$$

$$= 5 \times 10^{27}\ \text{Cu}\ m^{-4}$$

so that the flux

$$J = -D\left(\frac{dc}{dx}\right) = -(5.25 \times 10^{-13}) \times (-5 \times 10^{27})$$

$$= 26.25 \times 10^{14}\ \text{Cu}\ m^{-2}\ s^{-1}$$

Example 4.22 Show that under steady state the flux through a plane surface of length l and the surface concentration c_1 and c_2 is given by $D\frac{c_1 - c_2}{l}$, where D is the diffusion coefficient

Solution: Given: Diffusion through a plane surface, boundary conditions $c = c_1$ at $x = 0$, $c = c_2$ at $x = l$.

Let us begin with the Fick's second law for a plane surface given by the equation.

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2}\right) \tag{1}$$

Under steady state, D is constant and $\frac{dc}{dt} = 0$, therefore *eq*.1 reduces to

$$\frac{d^2c}{dx^2} = 0 \tag{2}$$

Integrating eq. 2 twice, a general solution of the same can be obntained as

$$C = Ax + B \tag{3}$$

where A and B are constants and can be determined by applying the boundary conditions, *i.e*, $c - c_1$ at $x = 0$ and $c = c_2$ at $x = l$. Substituting these values in *eq*.3 and solving for A and B, we obtain

$$\frac{c - c_1}{c_2 - c_1} = \frac{x}{l} \tag{4}$$

Finally, we can obtain the flux through the plane surface as

$$J = -D\frac{dc}{dx} = D\frac{c_1 - c_2}{l} \tag{5}$$

Example 4.23 Show that under steady state the flux through a cylindrical surface of radius r and the surface concentration c_1 and c_2 is given by $-\frac{2\pi Dt(c_2 - c_1)}{\ln(r_1/r_0)}$

Solution: Given: Diffusion through a cylindrical surface, boundary conditions $c = c_1$ at $x = r_0$ and $c = c_2$ at $x = r_2$.

Let us begin with the Fick's second law for a radially symmetric surface and isotropic medium given by the equation

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r}\right) \tag{1}$$

Under steady state condition, D is constant and $\frac{dc}{dt} = 0$, therefore *eq*. 1 reduces to

$$\left(\frac{d^2 c}{dr^2} + \frac{1}{r}\frac{dc}{dr}\right) = 0 \tag{2}$$

Integrating *eq*.2 twice, a general solution of the same can be obtained as

$$c = A \ln r + B \tag{3}$$

where A and B are constants and can be determined by applying the boundary conditios, *i.e*, $c = c_1$ at $r = r_0$ and $c = c_2$ at $r = r_1$. Substituting these values in *eq*.3, we obtain

$$c_1 = A \ln r_0 + B \tag{4}$$

$$c_2 = A \ln r_1 + B \tag{5}$$

and

so that $$c_2 - c_1 = A(\ln r_1 - \ln r_0)$$

or $$A = \frac{c_2 - c_1}{\ln r_1 - \ln r_0}$$

Substituting the value of A in *eq*. 4, we obtain

$$c_1 = \frac{c_2 - c_1}{\ln r_1 - \ln r_0} \ln r_0 + B$$

or $$B = c_1 - \frac{(c_2 - c_1)\ln r_0}{\ln r_1 - \ln r_0}$$

$$= \frac{c_1 \ln r_1 - c_1 \ln r_0 - c_2 \ln r_0 + c_1 \ln r_0}{\ln r_1 - \ln r_0}$$

$$= \frac{c_1 \ln r_1 - c_2 \ln r_0}{\ln(r_1/r_0)}$$

Substituting the value of A and B in *eq*. 3, we obtain

$$c = \frac{(c_2 - c_1)\ln r}{\ln (r_1/r_0)} + \frac{c_1 \ln r_1 - c_2 \ln r_0}{\ln (r_1/r_0)}$$

$$= \frac{c_2 \ln r - c_1 \ln r + c_1 \ln r_1 - c_2 \ln r_0}{\ln (r_1/r_0)}$$

$$= \frac{c_1 \ln (r_1/r) + c_2 \ln (r/r_0)}{\ln (r_1/r_0)} \tag{6}$$

Now, the flux through a cylindrical surface of radius r in time t is given by

$$J = -2\pi rtD \left(\frac{dc}{dr}\right)$$

$$= -\frac{2\pi Dt (c_2 - c_1)}{\ln (r_1/r_0)} \tag{7}$$

Example 4.24 Show that under steady state the flux through a spherical surface of radius r and the surface concentrations c_1 and c_2 is given by $-\dfrac{4\pi Dtr_0 r_1 (c_2 - c_1)}{(r_1 - r_0)}$

Solution: Given: Diffusion through a spherical surface, boundary conditions $c = c_1$, at $r = r_0$ and $c = c_2$ at $r = r_1$

Let us begin with the Fick's second law for spherically symmetric surface and isotropic medium given by the equation

$$\left(\frac{\partial c}{\partial t}\right) = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial c}{\partial r}\right) \tag{1}$$

Under steady state condition, D is constant and $\dfrac{dc}{dt} = 0$, therefore eq. 1 reduces to

$$\left(\frac{d^2 c}{dr^2} + \frac{2}{r} \cdot \frac{dc}{dr}\right) = 0 \tag{2}$$

or,

$$\frac{d}{dr}\left(r^2 \frac{dc}{dr}\right) = 0$$

Integrating eq. 2 twice, a general solution of the same can be obtained as

$$c = \frac{A}{r} + B \tag{3}$$

where A and B are constants and can be determined by applying the boundary conditions, i.e. $c = c_1$, at $r = r_0$ and $c = c_2$ at $r = r_1$. Substituting these values in eq. 3, we obtain

$$c_1 = \frac{A}{r_0} + B \tag{4}$$

$$c_2 = \frac{A}{r_1} + B \tag{5}$$

and

so that

$$c_1 - c_2 = \frac{A}{r_0} - \frac{A}{r_1} = A\left(\frac{r_1 - r_0}{r_0 r_1}\right)$$

or $$A = \frac{(c_1 - c_2)\, r_0 r_1}{(r_1 - r_0)}$$

Substituting the value of A in eq. 4, we obtain

$$c_1 = \frac{(c_1 - c_2) r_0 r_1}{(r_1 - r_0)} \frac{}{r_0} + B$$

$$= \frac{(c_1 - c_2) r_1}{(r_1 - r_0)} + B$$

or $$B = c_1 - \frac{(c_1 - c_2) r_1}{(r_1 - r_0)}$$

$$= \frac{c_2 r_1 - c_1 r_0}{(r_1 - r_0)}$$

Substituting the value of A and B in eq. 3, we obtain

$$c = \frac{(c_1 - c_2) r_0 r_1}{r(r_1 - r_0)} + \frac{(c_2 r_1 - c_1 r_0)}{r_1 - r_0}$$

$$= \frac{r_0 c_1 (r_1 - r) + r_1 c_2 (r - r_0)}{r(r_1 - r_0)} \tag{6}$$

Now, the flux through a spherical surface of radius r in time t is given by

$$J = -4\pi D t \left(\frac{dc}{dr}\right)$$

$$= -\frac{4\pi D t r_0 r_1 (c_2 - c_1)}{(r_1 - r_0)}$$

Example 4.25 The diffusion coefficient for *Li* in *Ge* at 500°C is of the order of $10^{-10} \text{m}^2/\text{s}$. What is its approximate distance of penetration in 1 hour?

Solution: Given $D \simeq 10^{-10}\ \text{m}^2/\text{s}$, $t = 1\ \text{hr} = 60 \times 60$ seconds, $T = 500°\text{C} = 773\ \text{K}$, $x = ?$

We know that the diffusion length in a medium is approximately given by

$$x = \sqrt{Dt}$$

Therefore, the distance of penetration corresponding to the given data is

$$x = \sqrt{10^{-10} \times 60 \times 60} = 0.6\ \text{mm} = 6 \times 10^{-4}\ \text{m}$$

Example 4.26 The diffusivity of gallium in silicon is $8 \times 10^{-13}\ \text{cm}^2/\text{s}$ at 1100°C and $1 \times 10^{-10}\ \text{cm}^2/\text{s}$ at 1300°C. (1) Determine the values of diffusion constant D_0 and activation energy Q, assuming the Arrhenius rate law is obeyed for this diffusion system, (2) calculate the diffusivity of the system at 1200°C.

Solution: Given: $D_{1100°C} = 8 \times 10^{-13}$ cm^2/s. $T_1 = 137$ K, $D_{1300°C} = 1 \times 10^{-10}$ cm^2/s, $T_2 = 1573$ K, and $R = 1.987$ cal mol^{-1} K^{-1} $D = ?$, $Q = ?$ and $D_{1200°C} = ?$

$\therefore$ Using Arrhenius equation in the $\log_{10}$ form

$$\log_{10} D = \log_{10} D_0 - \frac{Q}{2.303\ \text{RT}}$$

or

$$\log_{10} D = \log_{10} D_0 - \frac{Q\ \text{cal/mol}}{2.303 \times 1.987 \times T(K)} \qquad \text{(a)}$$

Thus, at 1100°C,

$$\log_{10} 8 \times 10^{-13} = \log_{10} D_0 - \frac{Q}{4.576 \times 1373} \qquad \text{(b)}$$

And at 1300°C,

$$\log_{10} 1 \times 10^{-10} = \log_{10} D_0 - \frac{Q}{4.576 \times 1573} \qquad \text{(c)}$$

Substracting eq. (c), from (b) we have

$$\log_{10} 8 \times 10^{-13} - \log_{10} 1 \times 10^{-10} = -Q(1.59 - 1.39) \times 10^{-4}$$

$$= -Q \times 0.20 \times 10^{-4}$$

or

$$0.9 - 13 + 10 = Q \times 0.20 \times 10^{-4}$$

Therefore

$$Q = \frac{2.1 \times 10^4}{0.20} = 105000\ \text{cal/mol}$$

$$= 105\ \text{kcal/mol}$$

Now, substituting the value of Q in eq.(c) we find

$$\log_{10} 10^{-10} = \log_{10} D_0 - \frac{105000}{4.576 \times 1573}$$

or

$$\log_{10} D_0 = -10 + 14.58 = 4.58$$

Therefore

$$D_0 = 38645\ \text{cm}^2/\text{s}.$$

(2) Given: $T = 1200 + 273 = 1473$K, $D_0 = 38645$ cm^2/s, and $Q = 10500$ cal/mol.

Now, substituting these values in eq.(a), we have

$$\log_{10} D \times 10^{-10} = \log_{10} 38645 - \frac{105000}{4.576 \times 1473}$$

$$= 4.58 - 15.57 = -10.99$$

Therefore

$$D = 1.02 \times 10^{-11}\ \text{cm}^2/\text{s}$$

Example 4.27 Consider the gas carburizing of a gear of 1018 steel (0.18 wt.%) at 927°C. Calculate the time necessary to increase the carbon content to 0.30 wt% at 0.60 mm below the surface of the gear. Assume the carbon content at the surface to be 1.00 wt.% and that the nominal carbon content of the steel gear before carburizing is 0.18 wt.% D(c in γ iron) at 927°C = 1.28×10^{-11}m^2/s.

Table 4.3 The error function

z	erf(z)	z	erf(z)
0.000	0.025	0.85	0.7707
0.025	0.0282	0.90	0.7970
0.05	0.0564	0.95	0.8209
0.10	0.1125	1.0	0.8427
0.15	0.1680	1.1	0.8802
0.20	0.2227	1.2	0.9103
0.25	0.2763	1.3	0.9340
0.30	0.3268	1.4	0.9523
0.35	0.3794	1.5	0.9661
0.40	0.4284	1.6	0.9763
0.45	0.4755	1.7	0.9838
0.50	0.5205	1.8	0.9891
0.55	0.5633	1.9	0.9928
0.60	0.6039	2.0	0.9953
0.65	0.6420	2.2	0.9981
0.70	0.6778	2.4	0.9993
0.75	0.7112	2.6	0.9998
0.80	0.7421	2.8	0.9999

Solution: Given: $C_0 = 0.18\%, C_x = 0.30\%, C_s = 1.0\%, x = 0.60\,\text{mm} = 6 \times 10^{-4}\text{m}$, $t = ?$

Also $$D_{927^\circ C} = 1.28 \times 10^{-11}\text{m}^2/\text{s}$$

Now using equation $\dfrac{C_s - C_x}{C_s - C_o} = erf\left(\dfrac{x}{2\sqrt{Dt}}\right)$ and substituting the given values, we find

$$\frac{C_s - C_x}{C_s - C_o} = erf\left[\frac{x}{2\sqrt{Dt}}\right]$$

or $$\frac{1.0 - 0.30}{1.0 - 0.18} = erf\left[\frac{6 \times 10^{-4}}{2\sqrt{1.28 \times 10^{-11}(t)}}\right]$$

or $$erf\left(\frac{83.85}{\sqrt{t}}\right) = \frac{0.70}{0.82} = 0.8536.$$

Here, $Z = \dfrac{83.85}{\sqrt{t}}$ and $erf\, Z = 0.8536$. From Table 4.3, the value of Z can be found by interpolation:

erf Z	Z
0.8427	1.0
0.8536	X

$$\frac{X - 1.0}{1.1 - 1.0} = \frac{0.8536 - 0.8427}{0.8802 - 0.8427}$$

0.8802 1.1

$$= \frac{0.0106}{0.0375} = 0.283$$

or $X = Z = 1.028$

or

Since, $Z = \frac{83.85}{\sqrt{t}} = 1.028$ or $t = 6653$ s $= 110$ m

Example 4.28 A gear made of 1020 steel (0.20 wt%C) is to be gas carburized at 927°C. Calculate the carbon content at 0.060 inch below the surface of the gear after a 10 *h* carburizing time. Assume the carbon content at the surface is 1.20 wt %. *D*(*C* in γ iron) at 927°C = 1.28×10^{-11} m^2/s.

Solution: Given: $C_o = 0.20\%$, $C_s = 1.2\%$, $t = 10\ h = 36 \times 10^3$s, $x = 0.060$ inch $= 0.060 \times 25.4 = 1.524$ mm

Also $D_{927°C} = 1.28 \times 10^{-11}$ m^2/s, $C_x = ?$

Again using equation $\frac{C_s - C_x}{C_s - C_o} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$ and substituting different values,

we find

$$\frac{C_s - C_x}{C_s - C_o} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

or $$\frac{1.20 - C_x}{1.20 - 0.20} = erf\left(\frac{1.524 \times 10^3}{2\sqrt{1.28 \times 10^{-11} \times 36 \times 10^3}}\right)$$

or $$1.20 - C_x = erf\,(1.1225).$$

Here, $Z = 1.1225$. Let us find the erf of this value by interpolation:

erf Z	Z
0.8802	1.1
X	1.1125
0.9103	1.2

$$\frac{X - 0.8802}{0.9103 - 0.8802} = \frac{1.1125 - 1.1}{1.2 - 1.1}$$

or $$\frac{X - 0.8802}{0.0301} = \frac{0.0025}{0.10} = 0.025$$

or $X = 0.8809$

or

Therefore, $1.20 - C_x = erf\,(1.1225) \times 0.8809$

or $C_x = 1.20 - 0.8809 = 0.32\%$

Example 4.29 At 927°C, a 1.2% carbon steel is getting decarburized for a duration of 5 hours in an atmosphere equivalent to 0% carbon at the surface of the steel. Determine the minimum depth upto which post machining is to be done, if the carbon content at the surface after machining should not be below 0.8%. D(C in γ iron) at 927°C = 1.28×10^{-11} m^2/s.

Solution: Given: $C_2 = 1.2\%$, $C_x = 0.8\%$, $C_s = 0\%$, $x = ?$, $t = 5\text{h} = 5 \times 3600 = 18000\text{s}$

Also $$D_{927^\circ\text{C}} = 1.28 \times 10^{-11}\text{m}^2/\text{s}$$

Now, using equation $\dfrac{C_s - C_x}{C_2 - C_s} = erf\left(\dfrac{x}{2\sqrt{Dt}}\right)$ and substituting the given values, we find

$$\frac{C_s - C_x}{C_2 - C_s} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

or $$\frac{0.0 - 0.80}{1.2 - 0.00} = erf\left(\frac{x}{2\sqrt{1.28 \times 10^{-11} \times 18 \times 10^3}}\right)$$

or $$erf\left(\frac{x}{9.6 \times 10^{-4}}\right) = \frac{0.80}{1.20} = -0.6666.$$

Here, $Z = \dfrac{x}{9.6 \times 10^{-4}}$ and $erf\, Z = 0.6666$. From Table 4.3, the value of Z can be found by interpolation:

erf Z	Z
0.6420	0.65
0.6666	*X*
0.6778	0.70

$$\frac{X - 0.65}{0.70 - 0.65} = \frac{0.6666 - 0.6420}{0.6778 - 0.6420}$$

or $$\frac{X - 0.65}{0.65} = \frac{0.0246}{0.0358} = 0.687$$

or $X = Z = 0.6843$

Therefore, $$Z = \frac{x}{9.6 \times 10^{-4}} = 0.6843$$

or $$x = 6.57 \times 10^{-4}\text{m}.$$

Thus the depth upto which machining is required is 0.66 mm.

Example 4.30 If boron is diffused into a thick slice of silicon with no previous boron in it at a temperature of 1100°C for 2 hours. What is the depth below the surface at which the concentration 10^{17} atoms/cm^3 if the surface concentration is 10^{18} atoms/cm^3? D(boron into silicon) $= 4 \times 10^{-13}\text{cm}^2/\text{s}$ at 1100°C.

Solution: Given: $C_0 = 0$, $C_x = 10^{17}$, $C_s = 100^{18}$, $T = 1373$ K, $t = 2h = 7200\text{s}$, $x = ?$

Also $$D_{1100^\circ\text{C}} = 4 \times 10^{-13}\text{cm}^2/\text{s}$$

Now, using equation $\dfrac{C_s - C_x}{C_s - C_o} = erf\left(\dfrac{x}{2\sqrt{Dt}}\right)$ and substituting the given values, we find

$$\frac{C_s - C_x}{C_s - C_o} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

or $$\frac{10^{18} - 10^{17}}{10^{18}} = erf\left(\frac{x}{2\sqrt{4 \times 10^{-13} \times 7200}}\right)$$

or $$erf\left(\frac{x}{2\sqrt{10.73 \times 10^{-5}}}\right) = 0.9$$

Here, $Z = \frac{x}{10.73 \times 10^{-5}}$ and $erf\, Z = 0.9$.

Now, making use of Table 4.3, let us find out the value of Z by interpolation:

erf Z	Z
0.8802	1.1
0.9000	X
0.9103	1.2

$$\frac{X - 1.1}{1.2 - 1.1} = \frac{0.9000 - 0.8802}{0.9103 - 0.8802}$$

or $X = Z = 1.658$.

Therefore, $$1.658 = \frac{x}{10.73 \times 10^{-5}}$$

or $$x = 1.24 \times 10^{-4} \text{ cm}.$$

Example 4.31 Determine the ratio of diffusion rate of silver in silicon at 1350°C to that 1100°C in a doping process. The activation energy Q for diffusion of silver in silicon is 154 kJ mol^{-1}.

Solution: Given: Temperature, $T_1 = 1350 + 273 = 1623$ K, $T_2 = 1100 + 273 = 1373$ K, Q = 154 kJ mol^{-1}, $D_1/D_2 = ?$

Making use of the diffusion equation in terms of molor and calorie units, *i.e*

$$D = D_0 \exp\left(-\frac{Q}{RT}\right)$$

we have,

$$D_1(\text{at } 1623) = D_0 \exp\left(-\frac{154 \times 10^3}{8.314 \times 1623}\right)$$

$$= D_0 \times 1.105 \times 10^{-5}$$

and $$D_2(\text{at } 1373) = D_0 \exp\left(-\frac{154 \times 10^3}{8.314 \times 1373}\right)$$

$$= D_0 \times 1.38 \times 10^{-6}$$

Therefore, $$\frac{D_1}{D_2} = 7.9868 \simeq 8$$

Example 4.32 The diffusion rate of A in B was studied at 500°C and 850°C for the same diffusion time. If the activation energy for diffusion of A in B is 57.16 kJ mol^{-1}. Determine the ratio of depth of penetrations x_1, and x_2 in the two experiments.

Solution: Given: Temperature, $T_1 = 500 + 273 = 773$ K, $T_2 = 850 + 273 = 1123$ K, $Q = 57.16$ kJ mol^{-1}, $t_1 = t_2 = t$, the depth of penetration ratio $\frac{x_1}{x_2} = ?$

Making use of the diffusion equation in terms of molar and calorie units, *i.e*,

$$D = D_0 \exp\left(-\frac{Q}{RT}\right)$$

We have

$$D_1(\text{at } 773) = D_0 \exp\left(-\frac{57.16 \times 10^3}{8.314 \times 773}\right)$$

$$= D_0 \times 1.772 \times 10^{-4}$$

and

$$D_2(\text{at } 1123) = D_0 \exp\left(-\frac{57.16 \times 10^3}{8.314 \times 1123}\right)$$

$$= 2.194 \times 10^{-3}$$

Further, making use of the equation related to penetration depth and diffusion rate, *i.e*

$$\frac{x}{2\sqrt{Dt}} = \text{constant } (K)$$

so that, at T_1 and T_2 with $t_1 = t_2$, we can write

$$\frac{x_1}{2\sqrt{D_1}K} = \frac{x_2}{2\sqrt{D_2}K}$$

or

$$\frac{x_1}{x_2} = \left(\frac{D_1}{D_2}\right)^{1/2}$$

$$= \left(\frac{1.372 \times 10^{-4}}{2.194 \times 10^{-3}}\right)$$

$$= 0.25$$

$$= \frac{25}{100} = \frac{1}{4}$$

$$\Rightarrow \quad x_1 : x_2 = 1 : 4$$

Example 4.33 Amorphous selenium used as a semiconductor material exhibits usual diffusion characteristics. The following is the set of experimental data for self-diffusion in amorphous selenium. Calculate D_0 and Q and comment on your results.

$T°C$	$D, m^2 s^{-1}$
35	7.7×10^{-16}
40	2.4×10^{-15}
46	3.2×10^{-14}
56	3.2×10^{-13}

Solution: Given:

$T°C$	$T(K)$	$D, m^2 s^{-1}$
35	308	7.7×10^{-16}
40	313	2.4×10^{-15}
46	319	3.2×10^{-14}
56	329	3.2×10^{-13}

Taking $R = 8.314$ J mol^{-1} K^{-1}, $D_0 = ?$, $Q = ?$

Substituting different in diffusion equation, we have

$$7.7 \times 10^{-16} = D_0 \exp\left(-\frac{Q}{8.314 \times 308}\right)$$

Similarly,
$$= D_0 \exp(-Q \times 3.905 \times 10^{-4}) \quad (1)$$

$$2.4 \times 10^{-15} = D_0 \exp(-Q \times 3.843 \times 10^{-4}) \quad (2)$$

$$3.2 \times 10^{-14} = D_0 \exp(-Q \times 3.771 \times 10^{-4}) \quad (3)$$

and
$$3.2 \times 10^{-13} = D_0 \exp(-Q \times 3.656 \times 10^{-4}) \quad (4)$$

Dividing eq. 4 by eq. 2, we obtain

$$\frac{3.2 \times 10^{-13}}{2.4 \times 10^{-15}} = \frac{\exp(-Q \times 3.656 \times 10^{-4})}{\exp(-Q \times 3.843 \times 10^{-4})}$$

or
$$133 = \exp[Q \times 10^{-4}(-3.656 + 3.843)]$$
$$= \exp(Q \times 0.187 \times 10^{-4})$$

Taking ln both sides, we obtain

$$\ln 133 = Q \times 0.187 \times 10^{-4}$$

or
$$Q = \frac{\ln 133}{0.187 \times 10^{-4}}$$
$$= 26.15 \times 10^4 \text{ Jmol}^{-1}$$
$$= 262 \text{ kJmol}^{-1}$$

Now substituting the value of Q in eq. 4, we obtain

$$3.2 \times 10^{-13} = D_0 \exp(-262 \times 10^3 \times 3.656 \times 10^{-4})$$

Taking ln both sides, we have

$$\ln(3.2 \times 10^{-13}) = \ln D_0 - 26.2 \times 3.656$$

or
$$\ln D_0 = \ln(3.2 \times 10^{-13}) + 95.787$$
$$= \ln 3.2 - 13 \ln 10 + 95.787$$

$$= 1.163 - 29.934 + 95.787$$
$$= 67.016$$

Therefore,

$$D_0 = 1.27 \times 10^{29} m^2 s^{-1}$$

Since, the graph is between ln D vs $1/T$, where ln D_0 is the intercept of the plot (corresponds to smallest reciprocal temperature). Thus, Q value is obtained from the slope between 1/56 and 1/40 because of non-uniform of temperature interval.

Example 4.34 A diffusion couple of 95% cu and 5% Zn and pure copper is annealed at 900°C for 50 hrs. The zinc concentration at a depth of 2 mm inside the copper bar was found to be 0.3% after the anneal. Determine the diffusion cofficient of zinc in copper.

Solution: Given: A diffusion couple with Cu = 90%C, Zn = 5% annealing temperature, $T = 900°C = 900 + 273 = 1173$ K, annealing time, $t = 50$ hrs $= 50 \times 60 \times 60 = 18 \times 10^4$ s , depth, $x = 2$ mm $= 2 \times 10^{-3}$ m, concentration at x, $C_x = 0.3\%$, $C_0 = 0\%$, $D = ?$

Since at. wt. of Cu = 63.546, and that of Zn = 65.38, therefore,

Atomic percent of Cu = 95/63.546 = 1.494980 = 95.1 a%

and atomic percent of Zn = 5165.38 $= \dfrac{0.076476}{1.571456} = 4.9\text{a}\% = \text{Cs}$

Now, using the expression representing the non-steady state solution of Fick's second law, i.e.

$$\frac{C_s - C_x}{C_s - C_o} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Substituting the given values we find

$$\frac{4.9 - 0.3}{4.9 - 0} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

or $$erf\left(\frac{x}{2\sqrt{Dt}}\right) = 0.94$$

Here $Z = \dfrac{x}{2\sqrt{Dt}}$ and $erf\,(z) = 0.94$

Making use of Table 4.3, the value of Z can be found by intrapolation

erf Z	Z	so that
0.9340	1.3	$\dfrac{X - 1.3}{1.4 - 1.3} = \dfrac{0.94 - 0.9340}{0.9523 - 0.9340}$
0.94	X	or $\dfrac{X - 1.3}{0.1} = \dfrac{0.0060}{0.00183}$
0.9523	1.4	or $X = \dfrac{60 \times 0.1}{183} + 1.3 = 1.33 = Z$

This gives us

$$\frac{x}{2\sqrt{Dt}} = 1.33$$

Squaring both sides and solving for D, we have

$$D = \frac{x^2}{4 \times (1.33)^2 \times t} = \frac{4 \times 10^{-6}}{4 \times (1.33)^2 \times 18 \times 10^4}$$

$$= 3.14 \times 10^{-12} \text{m}^2\text{s}^{-1}$$

Example 4.35 Compare the diffusivities of hydrogen, nitrogen and nickel in iron at 300K and explain the difference among the values.

Solution: Given: Temperature, $T = 300$K, compare D_H in Fe, D_N in Fe and D_{Ni} in Fe.

We know that at. Nos. of $H = 1$, $N = 7$ and $Ni = 28$. Further m. p of $H = -259°C$, $N = -210°C$ and Ni = 1453°C.

On the basis of above data, the diffusivity of H, N and Ni are in the order (of increasing $m.p$):

$$D_H \text{ in Fe} > D_N \text{ in Fe} > D_{Ni} \text{ in Fe}$$

Example 4.36 Calculate the rate at which a vacancy jumps in copper at 20°C. The activation barrier of the jump is 100 kJ mol^{-1}.

Solution: Given: The crystal is copper which has *fcc* structure, with $a = 3.61$ Å $= 3.61 \times 10^{-10}$ m. Temperature, $T = 20 + 273 = 293$ K, $Q = 100$ kJ mol^{-1}, $D = ?$

We can obtain the rate of diffusion by using diffusion equation,

$$\text{Rate of diffusion} = K \exp\left(-\frac{Q}{RT}\right) \quad (1)$$

where considering the diffusing constant K can be obtained by considering the diffusing plane of Cu as

$$a^2 = (3.61 \times 10^{-10})^2 = 13.03 \times 10^{-20} \text{ m}^2$$

There are two atoms in this area, therefore the number of atoms per unit area is

$$K = \frac{2}{13.03 \times 10^{-20}} = 15.35 \times 10^{22}/\text{m}^2$$

Subsisting all the values in eq. 1, we obtain

$$\text{Rate of diffusion} = 15.35 \times 10^{22} \exp\left(-\frac{100 \times 10^3}{8.314 \times 293}\right)$$

$$= 15.35 \times 10^{22} \times 1.485 \times 10^{-18}$$

$$= 2.28 \times 10^5 \text{ s}^{-1}$$

Review Problems

4.1 Show that the entropy of mixing equal numbers of two different kinds of atoms on one mole of fixed atomic sites is 5.76 J $mol^{-1}K^{-1}$.

4.2 Determine the fraction of atoms in a given solid with energies equal to or greater than 1.5 eV at 300 K and 1500 K.

Ans. 6.185×10^{-26}, 9.084×10^{-6}

4.3 If the enthalpy of formation of vacancy in aluminium is 0.7 eV, determine the ratio of vacancies in it when in equilibrium at 300 K to that produced by rapid quenching from 800 K. *Ans.* 4.44×10^{-8}

4.4 Determine the relative change in the density of copper due to vacancy at a temperature 1356 K, just below its melting point. The energy of formation of a vacancy in copper is 1 eV. *Ans.* 1.0001914 : 1

4.5 If the concentrtation of Schottky defect in an *fcc* crystal is 1 in 10^{10} at 300 K, determine the defect concentration at 1000 K. *Ans.* $1:10^3$

4.6 If the energy required to remove an ion pair from NaCl crystal is ~ 2 eV, determine the number of schottky imperfections present in the crystal at 300 K. *Ans.* $0.35 \times 10^6 cm^{-3}$

4.7 Determine the average energy required to create one Schottky imperfection in NaCl crystal, if the inter-ionic separation in it is 2.82 Å and density of Schottky imperfection at 300 K is 5×10^{11} m^{-3} *Ans.* 1.98 eV

4.8 Show that the number of Schottky defects in a monoatomic solid in equilibrium at a given temperature is given by

$$n = N \exp\left(-\frac{E_v}{kT}\right)$$

where E_v is the energy of formation of one vacancy.

4.9 Show that the number of Frenkel defects in a monoatomic solid in equilibrium at a given temperature is given by

$$n = (NN_i)^{1/2} \exp\left(-\frac{E_F}{2kT}\right)$$

where E_F is the energy of formation of one Frenkel defect.

4.10 If the average energy required to create one Frenkel defect in an ionic crystal is 1.4 eV, then determine the ratio of the number of Frenkel defects at 20°C and 300°C in 1gm of material. *Ans.* 1.30×10^{-6}

4.11 The Burgers vector of a mixed dislocation is $\frac{1}{2}$ [110]. The dislocation line lies along the [112] direction. Find the slip plane on which this dislocation

lies. Also, find the screw and edge components of the Burgers vector.
Ans. $(\bar{1}10)$; 1/6 [112] and 1/3 $[11\bar{1}]$.

4.12 Show that the dislocation reaction $\frac{a}{2}[\bar{1}10] \equiv \frac{1}{6}[\bar{2}11] + 1/6\ [\bar{1}2\bar{1}]$ is energetically favoured or not. *Ans.* Energetically favoured

4.13 In a simple cubic crystal ($a = 3$ Å), a positive edge dislocation 1 mm long climbs down by 1 μm. How many vacancies are lost or created?
Ans. 1.1×10^{10} created

4.14 Show that the energy of a screw dislocation is given as

$$E \sim lGb^2$$

where l, G and b respectively are length of the dislocation, shear modulus and the Burgers vector.

4.15 Determine the spacing between dislocations in a tilt boundary in *fcc* nickel, when the angle of tilt is 2°. *Ans.* 71.3Å

4.16 Show that under steady state the flux through a plane surface of length l and the surface concentrations C_1 and C_2 is given by

$$J = D\frac{C_1 - C_2}{l}$$

where D is the diffusion coefficient.

4.17 Show that under steady state the flux the through a cylinder surface of radius r and the surface concentrations C_1 and C_2 is given by

$$J = -\frac{2\pi Dt(C_2 - C_1)}{\ln(r_1/r_0)}$$

4.18 Show that under steady state the flux through a spherical surface of radius r and surface concentrations C_1 and C_2 is given by

$$J = -\frac{4\pi Dtr_0r_1(C_2 - C_1)}{r_1 - r_0}$$

4.19 The diffusion coefficient for *Li* in Ge at 500°C is of the order of 10^{-10} m^2/s. How much time it should take to penetrate a distance of 2 mm.
Ans. 400 seconds

4.20 What is the diffusion coefficient of Cu in Al at 550°C, assuming $Q = 121$ kJmol^{-1} and $D_0 = 0.25 \times 10^{-4}$ m^{2}s^{-1}? What is the approximate distance of penetration of Cu atoms in 1 hour? *Ans.* 5.25×10^{-13} m^{2}s^{-1}, 0.434 mm

4.21 If the ratio of diffusion rate of silver in silicon at 1350°C and 1100°C is found to be 8 in a doping process, determine the activation energy.
Ans. 154 kJ mol^{-1}

4.22 The diffusion rate of A in B was studied at 500°C and 850°C for the same diffusion time. The ratio of depth of penetrations x_1 and x_2 in two experiments were found to be 1 : 4. Determine the activation energy of diffusion of A in B. Ans. 57.16 kJ mol^{-1}

4.23 Consider the gas carburizing of a gear of 1020 steel at 927°C. Determine the time in minutes necessary to increase the carbon content to 40% at 0.50 mm below the surface. Assume that the carbon content at the surface is 0.90% and the steel has carbon content of 0.20%. *Ans.* 143 minutes

4.24 Consider the impurity diffusion of gallium into a silicon. If the gallium is diffused into a silicon wafer with no previous gallium in it at 1100°C for 3 hours. What is the depth below the surface at which the concentration is 10^{22} atoms/m^3 if the surface concentration is 10^{24} atoms/m^3 ?

Ans. 3.17×10^{-6}m

4.25 Calculate the rate of diffusion at which the vacancy jumps in copper at 300 K if the activation barrier of the jump is 100 kJ mol^{-1}.

Ans. $5.94 \times 10^{5} s^{-1}$

Multiple Choice Questions

4.1 The entropy of mixing equal numbers of two different kinds of atoms on one mole of fixed atomic sites in the units of $Jmol^{-1}K^{-1}$ is:

(a) 3.76 (b) 4.76 (c) 5.76 (d) 6.76

4.2 The fraction of atoms in a given solid with equal to or greater than 1.5 eV at 300 K is:

(a) 6.185×10^{-23} (b) 6.185×10^{-24}

(c) 6.185×10^{-25} (d) 6.185×10^{-26}

4.3 The fraction of atoms in a given solid with equal to or greater than 1.5 eV at 1500 K is:

(a) 9.084×10^{-5} (b) 9.084×10^{-6}

(c) 9.084×10^{-7} (d) 9.084×10^{-8}

4.4 The vacancy concentration 'n' in a monatomic solid at a certain temperature T is given by:

(a) $N \exp\left(-\frac{E_v}{kT}\right)$ (b) $N \exp\left(\frac{E_v}{kT}\right)$

(c) $N \exp\left(-\frac{E_v}{2kT}\right)$ (d) $N \exp\left(\frac{E_v}{2kT}\right)$

4.5 The concentration of Schottky imperfections 'n' in an ionic solid at a certain temperature T is given by:

(a) $N \exp\left(-\frac{E_p}{kT}\right)$ (b) $N \exp\left(\frac{E_p}{kT}\right)$

(c) $N \exp\left(-\frac{E_p}{2kT}\right)$ (d) $N \exp\left(\frac{E_p}{2kT}\right)$

4.6 The concentration of Frenkel imperfections 'n' in a monatomic solid at a certain temperature T is given by:

(a) $(NN_i)^{1/2} \exp\left(-\frac{E_F}{2kT}\right)$ (b) $(NN_i)^{1/2} \exp\left(\frac{E_F}{kT}\right)$

(c) $(NN_i)^2 \exp\left(-\frac{E_F}{2kT}\right)$ (d) $(NN_i)^2 \exp\left(\frac{E_F}{kT}\right)$

4.7 The concentration of Schottky defects in an *fcc* crystal is 1 in 10^{10} at 300 K. The value of concentration to be expected at 1000 K is:

(a) 1 in 10^{10} (b) 1 in 10^7 (c) 1 in 10^5 (d) 1 in 10^3

4.8 The energy required to remove a pair of ions from NaCl crystal is ~ 2 eV. The number of Schottky imperfections present per cubic centimeter crystal at 300 K is:

(a) 0.35×10^2 (b) 0.35×10^4

(c) 0.35×10^6 (d) 0.35×10^8

4.9 The density of Schottky defects in a certain sample of NaCl is 5×10^{11} m^{-3} at 300 K. If the inter-ionic separation is 2.82 Å, the average energy required to create one schottky defect is:

(a) 0.98 eV (b) 1.98 eV (c) 2.98 eV (d) 3.98 eV

4.10 The average energy required to create a Frenkel defect in an ionic crystal $A^{2+} B^{2-}$ is 1.4 eV. The ratio of the Frenkel defects at 300 K and 600 K in one gram of crystal material is:

(a) 1.316×10^{-6} (b) 2.316×10^{-6}

(c) 3.316×10^{-6} (d) 4.316×10^{-6}

4.11 In a simple cubic crystal ($a = 3$Å), a positive edge dislocation 1 mm long climbs up by 1 mm. The number of vacancies that are lost in the process is:

(a) 4.1×10^{10} (b) 3.1×10^{10}

(c) 2.1×10^{10} (d) 1.1×10^{10}

4.12 The approximate energy of a screw dislocation is given by:

(a) lGb (b) lGb^2 (c) lG^2b (d) l^2Gb

4.13 The approximate energy of an edge dislocation is given by:

(a) $\frac{lGb}{1-\nu}$ (b) $\frac{lGb^2}{1-\nu}$ (c) $\frac{lG^2b}{1-\nu}$ (d) $\frac{l^2Gb}{1-\nu}$

4.14 The number of slip systems in an *fcc* crystal is:

(a) 4 (b) 8 (c) 12 (d) 16

4.15 The number of slip systems in a *bcc* crystal is:

(a) 4 (b) 8 (c) 12 (d) 16

4.16 The number of slip systems in a *hcp* crystal is:

(a) 1 (b) 3 (c) 6 (d) 9

4.17 The diffusion coefficient for *Li* in *Ge* at 500°C is of the order of 10^{-10} m^2/s. The approximate distance of penetration of *Li* in *Ge* in 1 hour is:

(a) 6×10^{-2} m (b) 6×10^{-4} m

(c) 6×10^{-6} m (d) 6×10^{-8} m

4.18 The diffusion coefficient for *Li* in *Ge* at 500°C is of the order of 10^{-10} m^2/s. The time taken by *Li* to penetrate a distance of 2 mm in *Ge* is:

(a) 100 s (b) 200 s (c) 300 s (d) 400 s

4.19 Copper diffuses in aluminum at 550°C. The diffusion constant and the activation energy respectively are 0.25×10^{-4} m^2s^{-1} and 121 kJ mol^{-1}. The approximate distance of penetration of Cu in 1 hour is:

(a) 0.234 mm (b) 0.334 mm

(c) 0.434 mm (d) 0.534 mm

4.20 If the ratio of diffusion rates of silver in silicon at 1350°C and 1100°C is found to be 8, the activation energy in kJ mol^{-1} is:

(a) 154 (b) 254 (c) 354 (d) 454

4.21 In a doping process the activation energy for silver diffusing in silicon is 154 kJ mol^{-1}. The ratio of diffusion rate of silver in silicon at 1350°C to that 1100°C is:

(a) 2 (b) 4 (c) 6 (d) 8

4.22 The diffusion rate of *A* in *B* was studied at 500°C and 850°C. It was found that, for the same diffusion time, the depth of penetration x_1 and x_2 in two experiment were in the ratio of 1 : 4. The activation energy for diffusion of *A* in *B* in kJ mol^{-1} is:

(a) 37.16 (b) 47.16 (c) 57.16 (d) 67.16

4.23 The diffusion rate of *A* in *B* is studied at 500°C and 850°C for the same time. If the activation energy for this diffusion is 57.16 kJ mol^{-1}, the ratio of depth of penetration x_1 and x_2 in the two experiments is:

(a) 1 : 5 (b) 1 : 4 (c) 1 : 3 (d) 1 : 2

4.24 A gear made of 1020 steel (0.20 wt.% C) is to be carburized at 927°C. If the carbon content at the surface is 1.20 wt.% and D (C in γ iron) at 927°C = 1.28×10^{-11} m^2/s, the carbon content at 1.524 mm below the surface of the gear after a 10 hour carburizing time is:

(a) 0.12% (b) 0.22% (c) 0.32% (d) 0.42%

4.25 Boron is diffused into a thick slice of silicon with no previous boron in it at a temperature of 1100°C for 2 hours. If the surface concentration is 10^{18} atoms/cm^3 and D (boron into silicon) = 4×10^{-13} cm^2/s at 1100°C, the depth below the surface at which the concentration is 10^{17} atoms/cm^3 is:

(a) 1.24×10^{-4} cm (b) 1.24×10^{-5} cm
(c) 1.24×10^{-6} cm (d) 1.24×10^{-7} cm

Answers

1. (c)	2. (d)	3. (b)	4. (a)	5. (c)	6. (a)	7. (d)
8. (c)	9. (b)	10. (a)	11. (d)	12. (b)	13. (b)	14. (c)
15. (c)	16. (b)	17. (b)	18. (d)	19. (c)	20. (a)	21. (d)
22. (c)	23. (b)	24. (c)	25. (a)			